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| Page | Line | | | |
|------|------|------------------------|--|---|
| | | | "CH ₂ :C·CH ₂ ·CH ₃ " | "CH ₂ :C·OH ₂ ·CH ₃ " |
| 1245 | 5 | for | $\begin{array}{c} \\ \text{C} - \text{CH}_3 \end{array}$ | read $\begin{array}{c} \\ \text{O} - \text{CO} \end{array}$ |
| 2001 | 25 | for "has" read "have." | | |

which becomes of increasing importance as the hydration diminishes.

Summary.—1. It has been found possible to construct viscometers in which the flow of liquid is so slow that, for solutions whose viscosity differs little from that of water, Poiseuille's law is obeyed with an error of not more than one part in 10,000. The methods used in testing the viscometers are described.

2. A correction has been introduced for the variation in surface effects when different liquids are used in the viscometer.

3. Determinations of density and viscosity have been carried out with lithium nitrate solutions at 0°, 18°, and 25° over a large range of concentration.

4. The formula of Grüneisen is found not to represent the phenomena of dilute solution.

5. A method of calculating the viscosity of salt solutions from their hydration numbers, or vice versa, has been described. The application of this method to the viscosities of lithium nitrate solutions at 18° gives results consistent with the estimates of ionic hydration made by other observers.

6. The application of the method to other salts is discussed.

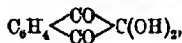
I am greatly indebted to Mr. D. H. Nagel and Mr. H. B. Hartley for much valuable advice and encouragement during the progress of this work.

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CCXII.—*Triketohydrindene Hydrate.*

By SIEGFRIED RUEHMANN.

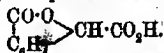
In a recent paper (this vol., p. 1438) it was shown that the condensation product of α -hydrindone with *p*-nitrosodimethylaniline, on treatment with dilute sulphuric acid, decomposes with the formation of triketohydrindene hydrate. Its formula was represented thus:



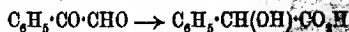
according to which the elements of water are united with the 2-ketonic group of triketohydrindene. There cannot be any doubt as to the correctness of this formula, because the union of water with any other ketonic group of the triketons would produce a coloured

compound owing to the proximity of two ketone groups whereas triketohydrindene hydrate is colourless, it is also 1,2-diketohydrindene, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH_2$. Further evidence in support of the above formula is the fact that the hydrate, on treatment with phosphorus pentachloride, is transformed into the colourless 2:2-dichloro-1:3-diketohydrindene, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CCl_2$. Triketohydrindene also forms additive products with other substances, such as guanidine or benzamidine, which are colourless, and therefore are to be represented by formulae similar to that of triketohydrindene hydrate. The hydrate further reacts with hydrogen cyanide to yield the unstable cyanohydrin, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C(OH) \cdot CN$.

A closer study of the remarkable behaviour of potassium hydroxide towards the hydrate which was described previously (*loc. cit.*, p. 1448) led to the following result. The reaction proceeds in three distinct phases, which are indicated by colour changes. On the addition of the alkali to the crystals of the hydrate, they turn yellow and then dissolve to form a yellow solution; this subsequently becomes blue, even at the ordinary temperature, if the alkali is concentrated. The blue colour, however, is very fugitive, and disappears on dilution with water to yield a colourless solution. On using dilute potassium hydroxide (about 15 per cent.), the blue colour does not appear unless the temperature is raised immediately after the addition of the alkali to the hydrate. The colourless alkaline solution, which represents the last phase of the reaction, contains the potassium salt of α -carboxymandelic acid, $CO_2H \cdot C_6H_4 \cdot OH(OH) \cdot CO_2H$, because, on treatment with dilute sulphuric acid, it yields phthalidecarboxylic acid,

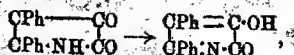


The formation of this acid leads to the conclusion that, under the influence of the alkali, the five-carbon ring of triketohydrindene ruptures with the formation of phenylglyoxal- α -carboxylic acid, $CO_2H \cdot C_6H_4 \cdot CO \cdot CHO$, which finally undergoes the change to phthalidecarboxylic acid. This behaviour resembles in every respect the change which, by the action of alkalis, phenylglyoxal undergoes to mandelic acid:

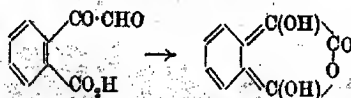


The result arrived at in examining the behaviour of triketohydrindene hydrate towards potassium hydroxide supports the view which was expressed before (*loc. cit.*) concerning the product of the action of ammonia on the triketone. The formation of phenylglyoxal- α -carboxylic acid is to be regarded as the first change of the triketonic compound

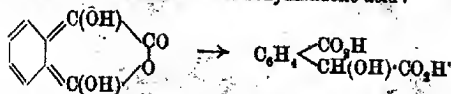
which is produced by the alkali and the view follows, also, from the fact that the yellow alkaline liquid reduces Fehling's solution. The explanation of the intermediate phase of the reaction which is characterized by the blue colour of the alkaline solution is difficult, because the solution readily loses its colour, and passes into the final phase of the reaction. It is, therefore, only from analogy to the changes which the diketopyrrolines and the compounds with similar structure undergo, on treatment with alkalis, that a view can be expressed concerning the nature of the blue product. The blue solution which, for example, diketodiphenylpyrrolone yields with potassium hydroxide was explained (Trans., 1909, 95, 984) by the change into its tautomeric form:



which contains a phenolic group and has an *o*-quinonoid structure. A similar arrangement may be assumed to exist in the potassium compound which is formed in the second phase of the action of the alkali on triketohydrindene hydrate. Accordingly, phenylglyoxal-*o*-carboxylic acid, which is first produced, undergoes ring formation, thus:



in which, also, phenolic groups are associated with an *o*-quinonoid structure. A substance with this constitution may be supposed to yield blue salts with alkalis. These, like the corresponding salts of the diketopyrrolines, are unstable, and, on dilution with water, are transformed into the salts of *o*-carboxymandelic acid:



The further study of triketohydrindene hydrate led to results which appear to be of great interest. It was found that a deep blue colour is produced on warming a mixture of aqueous solutions of this compound and an aliphatic or an aliphatic-aromatic amino-acid which contains the amino-group in the side-chain. As shown below, this reaction has been successfully applied to a number of α -amino-acids, but as yet only two β -amino-acids have been tested, and they were found to differ markedly from the α -amino-acids in their behaviour towards the triketone, because with them the colour reaction takes place less readily, and in the case of β -amino- β -phenylpropionic acid is far less intense than with the corresponding α -amino-acids. No

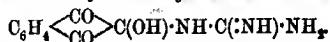
coloration, however, is produced by the triketone in solutions of aromatic amino-acids which contain the amino-group in the nucleus, nor does it occur with substituted amino-acids, such as phenylglycine or hippuric acid. On the other hand, triketohydrindene hydrate gives a blue reaction with peptone, and this fact in the light of the results indicated above leads to the conclusion that in the peptones, compounds occur which contain the free amino-group of amino-acids.

The same coloration is produced in normal human urine on warming it with an aqueous solution of the reagent. This behaviour agrees with the observations of Abderhalden and Pregl (*Zeitsch. physiol. Chem.*, 1905, 46, 19; see also Abderhalden and Schittenhelm, *ibid.*, 1906, 47, 1396), according to which the urine contains a protein-like substance. The authors showed that it does not contain free amino-acids, but that these are formed from it on hydrolysis.

EXPERIMENTAL.

Triketohydrindene hydrate was prepared in the manner described before (*loc. cit.*) by warming slightly the product of the action of *p*-nitrosodimethylaniline and α -hydrindone with dilute sulphuric acid; its extraction from the dark solution which is formed, is more conveniently effected by ethyl acetate than by ether on account of its greater solubility in that solvent.

Additive Product of Triketohydrindene with Guanidine,



This is formed by adding triketohydrindene hydrate (1 gram), dissolved in water, to an aqueous solution of guanidine, obtained from its chloride (0.6 gram) and the calculated quantity of potassium hydroxide. The mixture turns red and soon deposits a colourless solid, which is insoluble in water, alcohol or benzene; it does not melt, but begins to darken at about 190° and finally becomes black:

0.2015 gave 0.4045 CO_2 and 0.0740 H_2O . C = 54.75; H = 4.08.

0.1945 „ 32.6 c.c. N_2 at 20° and 754.5 mm. N = 19.02.

$\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ requires C = 54.79; H = 4.11; N = 19.18 per cent.

On heating the compound with water for some time, slight decomposition takes place, and a small quantity dissolves to yield a red solution.

Additive Product of Triketohydrindene with Benzamidine.

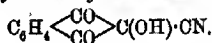

This is prepared in a similar way to the former substance, namely, by adding sodium carbonate to the mixture of triketohydrindene hydrate (1.2 grams) and benzamidine hydrochloride (1 gram) dissolved in hot water. A white solid is soon precipitated, which is insoluble in water; it is sparingly soluble in boiling alcohol, but does not separate from the solution without the addition of water, when colourless prisms are formed, which darken at about 200° and decompose at $229-230^\circ$ with evolution of gas:

0.2011 gave 0.5050 CO_2 and 0.0805 H_2O . C = 68.49; H = 4.44.

0.2051 „ 17.8 c.c. N_2 at 17° and 762 mm. N = 10.10.

$\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$ requires C = 68.58; H = 4.29; N = 10.0 per cent.

This substance is insoluble in sodium carbonate; it is decomposed by hot potassium hydroxide with the formation of benzaldehyde.

Additive Product of Triketohydrindene with Hydrogen Cyanide,


Whilst the additive compounds mentioned above are fairly stable, the *cyanohydrin*, which triketohydrindene hydrate forms with hydrogen cyanide, is readily decomposed. It is obtained by mixing the triketone hydrate (0.5 gram), dissolved in water, with potassium cyanide (0.5 gram), and then adding dilute hydrochloric acid to the deep red solution which is produced. The colour disappears and pale brown needles separate which sinter and darken at about 120° , and at 148° melt with evolution of gas. The compound dissolves in boiling water, but at the same time decomposes. For analysis, the crystals formed in the reaction were washed with cold water and dried in a vacuum desiccator over sulphuric acid:

0.2053 gave 13.8 c.c. N_2 at 18° and 749 mm. N = 7.64.

$\text{C}_{10}\text{H}_8\text{O}_2\text{N}$ requires N = 7.49 per cent.

Action of Phosphorus Pentachloride on Triketohydrindene Hydrate.

On mixing the triketone hydrate (1 mol.) with phosphorus pentachloride (2 mols.), no reaction takes place at the ordinary temperature; at 100° , the mixture evolves hydrogen chloride and assumes a red colour, which is probably due to the removal of water and the formation of triketohydrindene. The action proceeds more readily if phosphoryl chloride is used together with phosphorus pentachloride; on warming,

the whole solution is mixed with a little alcohol, which is then poured on ice, when an oil is precipitated which soon solidifies. The solid is washed with light petroleum, which removes a yellow product, whilst a colourless substance remains undissolved. This is readily soluble in hot dilute alcohol, and, on cooling, crystallises in colourless plates. The yield is poor owing to the formation of the yellow by-product. The compound was identified as 2:2-dichloro-1:3-diketohydrindene, $C_8H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} COCl_2$, by the melting point, $124-126^\circ$, and its chemical behaviour (compare Zincke and Gerland, *Ber.*, 1888, 21, 2390).

Formation of Phthalidecarboxylic Acid from Triketohydrindene Hydrate.

The action of potassium hydroxide on the triketone hydrate was described in a previous paper (this vol., p. 1448) and more fully on p. 2026. It was stated that the final phase of the reaction yields a colourless solution. This, when treated with an excess of dilute sulphuric acid and digested on the water-bath for an hour, contains phthalidecarboxylic acid, $C_8H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown CO \end{smallmatrix} CH \cdot CO_2H$. It is isolated from the acid solution by extraction with ether, and, on evaporation of the ether, is left as a white solid. This readily dissolves in hot water, and, on cooling, crystallises in colourless plates melting at $150-151^\circ$. The yield is almost theoretical. (Found: C=60.70; H=3.37. Calc., C=60.67; H=3.37 per cent.)

The compound is identical with the acid which Zincke (*Ber.*, 1894, 27, 743), in the course of his researches on the action of bleaching powder on quinones, obtained from monochloro- β -naphthoquinone as well as from isocoumarincarboxylic acid.

Action of Triketohydrindenehydrate on Amino-acids.

On mixing a slightly warmed aqueous solution of triketohydrindene hydrate and glycine, an intense blue colour develops immediately, and, after a short time, a dark solid separates. The same behaviour is shown by all the α -amino-acids which I have been able to obtain; several of them I owe to the kindness of Dr. Hopkins, whom I have also to thank for the interest he took in the progress of the work. The reaction has been applied to alanine, valine, leucine, tyrosine, to α -amino- β -phenylpropionic, aspartic, and glutamic acids, to tryptophan and cystine. Owing to the fact that the latter compound is sparingly soluble in water, it must be boiled with a solution of the triketone hydrate; in all the other cases,

the reaction with triketone hydrate, which is still perceptible with triketone, and reaction with triketone hydrate, which is still perceptible on slightly warming pyridine with a solution which contains 1 part of triketone hydrate dissolved in 15,000 parts of water. In the same dilution the reagent yields with ammonia a yellow coloration, whereas the colour is red, or reddish-violet, on using more concentrated solutions (compare this vol., p. 1447). The shade of the blue coloration that is produced shows but slight variations with the different α -amino-acids. Of the β -amino-acids only two have been tested, namely, β -aminopropionic acid and β -amino- β -phenylpropionic acid. The latter, which was prepared according to Posner's directions (*Ber.*, 1903, 36, 4313) by the action of hydroxylamine on cinnamic acid, differs remarkably from its isomeride, α -amino- β -phenylpropionic acid, in its behaviour towards triketohydrindene hydrate; no colour is produced on mixing the reagents dissolved in hot water. A faint violet coloration, however, develops if the solution is boiled for some time; on the other hand, the corresponding α -amino-acid readily reacts with the triketonic compound to yield a deep blue colour. The difference between α - and β -aminopropionic acids in their behaviour towards the reagent, although not so striking as with the former isomeric acids, is yet apparent, especially as regards the rapidity of the reaction, which in this case, also, is greater with the α -amino-acid. It is, however, necessary to examine a larger number of the β -amino-acids before, by means of the reagent, a general distinction between the two groups of amino-acids can be established. Neither phenylaminoacetic acid (phenylglycine) nor hippuric acid yield a coloration with the triketone hydrate, even on boiling the aqueous solutions of the mixtures, and this result indicates that the reaction depends on the amino-group of the amino-acid being intact. Aromatic amino-acids which contain the amino-group in the nucleus, for example, α -aminobenzoic acid, also do not respond to the test.

The chemical nature of the colour reaction has not yet been ascertained, but experiments in this direction are already in progress, and will be recorded shortly.

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CCXIII.—*The Vapour Pressures and Molecular Volumes of the Mercuric Halides and the Relations between Atomic Volumes of Elements Before and After Combination.*

By EDMUND BRIDGES RUDHALL PRIDEAUX.

THE present investigation has the aim of comparing the volumes of liquid elements with those of their liquid compounds. As comparison temperatures the boiling points under atmospheric or other equal pressures have been retained. The results of Young and others show that at vapour pressures below one atmosphere it is a matter of indifference whether equal pressures or corresponding pressures are chosen for the above comparison. The procedure of finding atomic volumes at the boiling point is too well known to need description. It has been departed from in several particulars.

(1) No attempt has been made to tabulate difference of molecular volume, the ratios only being compared.

(2) No experimentally inaccessible atomic volumes, such as those of carbon and hydrogen, have entered into the calculation.

(3) The effect of structure on the molecular volume has been as far as possible eliminated by considering only simple compounds, in which there is not more than one multivalent element.

The term atomic or molecular volume at any pressure is used throughout to denote the total volume occupied by the gram-atom or gram-molecule liquid at such a temperature that its vapour pressure is that specified. Under these conditions the ratio between the specific volumes at, for example, 760 and 200 mm. pressure is a constant for liquids which are not associated or dissociated.

For example, $\frac{V_M(760)}{V_M(200)}$ is, for: C_6H_6 1.050, PCl_3 1.050, $C_2H_4Br_2$ 1.048, O_2 1.048, HCl 1.049. Instances could be multiplied. Associated and monatomic liquids: H_2O 1.030, CH_3CO_2H 1.041, Hg 1.012, A 1.014 (760–400), the normal value for this pressure interval being 1.028.

These relations may be connected in the following way with theories involving the conception of "co-volume." The term is used throughout as generally to mean the volume through which the molecules have motion relatively to one another, sometimes called "free ether," as distinguished from the "bound ether" or interatomic space, which, together with the volumes of the atoms themselves, makes up the " b " of van der Waals' equation (Clausius) which no other atom can penetrate.

Now, if we imagine an ideal and normal liquid expanding from the condition in which the co-volume is zero (which as will be shown, is probably not in most cases -273°), the vapour pressure will increase at the same time, and since the pressure is a function of the temperature and the increase of co-volume also a function of the temperature, the increase of co-volume may be expressed as a function of the pressure.

Thus if V_p and V_o are the volumes of liquid at " p " and zero pressure:

$$V_p = V_o[1 + \phi(p)],$$

$\phi(p)V_o$ being therefore the co-volume at " p ."

For another liquid, also expanding between " o " and " p ":

$$V_p' = V_o'[1 + \phi'(p)].$$

At a higher pressure, p_1 , the volumes become $V_o[1 + \phi(p_1)]$ and $V_o'[1 + \phi'(p_1)]$ respectively.

But as shown above, in the case of normal liquids:

$$\frac{V_o[1 + \phi(p_1)]}{V_o[1 + \phi(p)]} = \frac{V_o'[1 + \phi'(p_1)]}{V_o'[1 + \phi'(p)]};$$

that is

$$\frac{V_o[1 + \phi(p_1)]}{V_o[1 + \phi(p)]} = \frac{V_o'[1 + \phi'(p_1)]}{V_o'[1 + \phi'(p)]}.$$

Therefore $\phi(p) = \phi'(p)$ and $\phi = \phi'$.

(1) The increase of co-volume is the same function of " p " for all these liquid. Assuming that the same law of expansion holds down to the lowest, and eventually, zero pressure:

$$\frac{V_o[1 + \phi(p)]}{V_o[1 + \phi(p)]} = \frac{V_o}{V_o}.$$

(2) The co-volumes $V_o\phi(p)$ and $V_o'\phi(p)$ at any pressure are proportional to the actual volumes of the molecules V_o and V_o' .

(3) The ratios between the volumes of the liquids at equal vapour pressures are equal to the ratios between the actual volumes of the molecules.

As soon as the vapour becomes so dense that the specific molecular attraction begins to have an effect in that phase, the nature of the relation between increments of vapour pressure and volume will probably change, and $\phi(p)$ take another form. By taking this into account, Mills (*J. Physical Chem.*, 1902, 6, 209; 1904, 8, 383, 593)

has deduced the formula $\frac{q}{\sqrt{d} - \sqrt{D}} = \text{constant}$ for a series of normal

liquids at different temperatures (q = inner heat of vaporisation of 1 gram liquid; d and D = densities of liquid and vapour). This equation holds up to the critical temperature. It can be shown that at temperatures so low that \sqrt{D} may be left out of account compared

with \sqrt{d} (considerably below the boiling point under atmospheric pressure), Mills' equation necessarily leads to the regularity mentioned above. For consider two liquids, A and B , at two pressures, P and P' , and let Q be the total molecular latent heat of vaporization and R the gas constant. To the values of P , T , Q and d for the two liquids assign the symbols:

$$\begin{array}{cccccc} P & T_A & T_B & Q_A & Q_B & d_A & d_B \\ P & T_A & T_B & Q_A & Q_B & d_A & d_B \end{array}$$

Then for each liquid, by Mills' formula:

$$\frac{Q - RT \sqrt{d}}{Q - RT' \sqrt{d}} = 1 \quad (1)$$

Multiply by T/T' :

$$\frac{Q/T - R \sqrt{d}}{Q/T' - R \sqrt{d}} = \frac{T}{T'} \quad (2)$$

Divide equation (2) for A by (2) for B :

$$\frac{Q_A/T_A - R}{Q_B/T_B - R} \times \frac{Q_B/T'_B - R}{Q_A/T'_A - R} \times \sqrt{\frac{d'_A d_B}{d_A d'_B}} = \frac{T'_A T_B}{T_A T'_B}$$

But for normal liquids:

$$\frac{Q_A}{T_A} = \frac{Q_B}{T_B}, \text{ etc.}$$

Also

$$\frac{T_A}{T'_B} = \frac{T_A}{T'_B} + c(T'_A - T_A),$$

where " c " is very small, not greater than 0.0005 for the most dissimilar liquids: therefore

$$\sqrt{\frac{d'_A}{d_A}} = \sqrt{\frac{d'_B}{d_B}} \quad \frac{d'_A}{d_A} = \frac{d'_B}{d_B}$$

This relation can only be deduced from Mills' formula at temperatures at which the density of the vapour may be neglected. A recalculation of the constant (Mills, *J. Physical Chem.*, 1909, 13, 512) has proved that the formula holds with the greatest accuracy in this region.

The assumption, then, that $\phi(p)$ remains constant down to the lowest pressure is in accordance with the above theory of molecular attraction, and with the facts of expansion down to the lowest vapour pressure at which liquid volumes have been compared.

The volumes at zero pressure could be found by extrapolation if the pressures were known with sufficient accuracy. The laws of expansion of liquids lead to an ideal state of zero co-volume for a perfect liquid, just as the laws of expansion of gases lead to the state of an ideal gas at the absolute zero.

In the case of liquids, however, it does not seem probable that

the zero of pressure should occur at the same temperature in each case. The necessity for a normal zero in each case has already been felt in explaining the deviations from the reduced equation of condition (Young, *Stoichiometry*, p. 237).

If it were possible, then, to obtain the liquid volumes of non-associated elements and compare them with the volumes of liquid non-associated compounds all at the same pressure, the ratios of these volumes would correspond with the ratios of the actual volumes of the molecules, the expansion or contraction on combination being thus discoverable.

Owing, however, to the scarcity of data, a direct comparison of this sort is in few cases possible, and where it can be made, most of the expansions are found to be not quite normal. The degree to which these irregularities influence the ratios will appear from the experimental data.

EXPERIMENTAL.

Materials.—The mercuric chloride was re-sublimed in a current of dry chlorine. Several analyses were made both of the freshly prepared salt and that which had been boiled for some time in the air, or heated in the dilatometer. The mercury was determined as mercuric sulphide, and the chlorine as silver chloride, and the results were satisfactory.

The mercuric bromide prepared to order by Hopkin and Williams gave satisfactory results on analysis, and was employed without further treatment in some cases. A sample redistilled with a little bromine gave identical results on analysis and in the dilatometer.

The mercuric iodide was also Hopkin and Williams' preparation. It was analysed by electrodeposition on a silver-plated platinum basin cathode, and gave theoretical results. It was afterwards redistilled to remove traces of a non-volatile impurity, which apparently did not affect the analysis, but made the liquid surface difficult to locate in the dilatometer.

Dilatometers.—These were of fused silica, and were supplied by the Silica Syndicate. They were graduated as required by a diamond fixed in place of the needle on a divider, and calibrated with mercury in the usual way. The bulbs were cylindrical, of about 2 c.c. capacity. The stems were graduated in mm., and each cm. length held from 0.02 to 0.03 c.c.

Thermometers.—Three nitrogen-filled mercury thermometers were used:

- (1) Reading up to 600° in 3°; standardised at the National Physical Laboratory.

(2) To 600° in 2°, and (3) to 500° in 1°; these were standardised by comparison with (1).

Thermostats.—For temperatures up to 260° a bath of paraffin wax was used, and for these as well as higher temperatures the vapours of liquids boiling under various pressures were employed. These have been tabulated by Landolt and Börnstein from the measurements of Ramsay and Young as follows:

| | |
|----------------|-----------------------|
| 260—280° | Monobromonaphthalena. |
| 280—304° | Diphenylamine. |
| 360° | Mercury. |

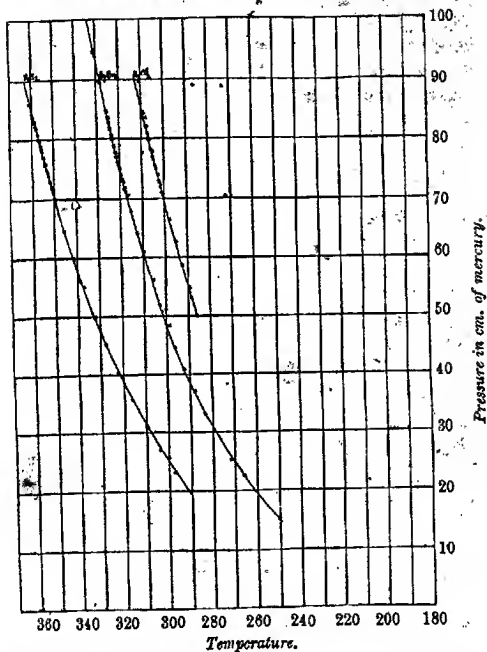
For the interval 310—339°, anthracene, boiling under diminished pressure, was used instead of the vapour of mercury.

The paraffin wax thermostat consisted of a large beaker of resistance glass jacketed with asbestos and heated by a gas flame from below. Additional heat was supplied by an electrically heated frame of iron wire in the liquid, which was stirred by a brass fan wheel at the bottom, and automatically regulated by a glass cylinder holding about 150 c.c. of air, which extended to the bottom of the liquid, and communicated by means of a capillary tube with a mercury gas regulator. The temperature could by this means easily be kept constant to a few tenths of a degree. The thermometers, etc., were not directly in contact with the liquid, but were protected by tubes of combustion glass.

The vapour-bath first used had somewhat the form of a Liebig's condenser. To a vertical glass tube open at each end was sealed an outer tube above and below. The vapour of the boiling liquid filled the space between the tubes. The liquid was contained in two side-bulbs joined to the lower end of the outer tube at an angle of about 45°. It was heated by burners and also electrically by platinum spirals. The electrical heating was used mainly to prevent bumping at low pressures. The lower part of the apparatus was protected by an asbestos box packed with magnesia. In order to save time, this was electrically heated by nickel wire. The upper part was shielded by movable rings of asbestos covered with felt. It was found that this form had several disadvantages when used for high boiling liquids—the radiation is large compared to the evaporating surface, and the dead space between the internal seal and junction of side-tubes adds considerably to the time required to send the ring of condensing vapour a sufficient distance up the tube. For the purpose in hand, however, the apparatus had the great advantage of allowing the introduction of dilatometers from below, so that they could be heated from the top downwards, thus avoiding the sometimes troublesome distillation of drops of liquid to the upper part of the tube.

In the form of vapour-bath afterwards used, the dilatometer was introduced from above into a glass tube about 2 cm. in diameter, which was heated by the vapour of a liquid boiling in a much larger bulb, the lower end of the inner tube being protected from the radiation of the superheated liquid by the well-known method recommended for thermometers in Young's *Fractional Distillation*. The vapour space was connected through a reservoir of about

Vapour pressures of mercuric chloride, bromide, and iodide.



10 litres capacity and a drying tower to a water exhaust pump or pressure pump as the case might be. The pressures were read on a mercury manometer attached to a wooden metre scale.

Vapour Pressures.—These were regulated and read by means of the air reservoir and mercury manometer already mentioned. The liquids were boiled under various pressures in a combustion glass tube. The sides of the tube were protected from overheating by horizontal pieces of asbestos board, and from cooling radiation by

slip rings of asbestos covered with felt. The liquid was in every case boiled at such a rate that the thermometer column was completely immersed in the vapour. The bulb of the thermometer was covered with asbestos.

The results are tabulated below, and also shown in the figure.

The experimental points are indicated by X. A few vapour pressures at lower temperatures by Wiedemann, Stelant, and Niederschulte (*Ber. deut. physikal. Ges.*, 1905, 7, 159) are indicated as follows: mercuric chloride by circles, mercuric bromide by crosses, and mercuric iodide by circles. Most of these were deduced from the loss in weight when a measured quantity of air was passed over the solid at the temperature in question, and some by observing the pressure and temperature when the compounds were suddenly sublimed into a cooled tube. The curve so obtained ought not, of course, to be continuous with that of the vapour pressures of the liquids; but the observations in the neighbourhood of the melting point are not numerous enough for any discontinuity to be observed. The three observations recorded (by the authors quoted above) at higher temperatures do not agree with the present results, probably because the method they employed was not so suitable for higher temperatures. The pressures used for the subsequent calculations are those read from the manometer at 16°0.

The following are the vapour pressures (to the nearest millimetre) corresponding with the corrected temperatures. The index numbers to the right of the pressures refer to different series of experiments.

| Mercuric Chloride. | | | | Mercuric Bromide. | | | | Mercuric Iodide. | | | |
|--------------------|-------|------|-------|-------------------|-------|------|-------|------------------|-------|-------|-------|
| P. | t. | P. | t. | P. | t. | P. | t. | P. | t. | | |
| (mm.) | | | | (mm.) | | | | (mm.) | | | |
| 844, | 309.0 | 751, | 303.0 | 947, | 331.0 | 729, | 318.3 | 861, | 360.5 | 851.6 | |
| 836, | 308.2 | 741, | 302.5 | 897, | 328.4 | 728, | 317.8 | 829, | 358.8 | 720, | 350.8 |
| 822, | 307.5 | 730, | 302.7 | 847, | 325.4 | 719, | 317.3 | 821, | 358.0 | 720, | 350.5 |
| 820, | 308.1 | 724, | 301.5 | 836, | 324.9 | 719, | 317.8 | 819, | 357.9 | 711, | 350.1 |
| 816, | 306.8 | 719, | 301.9 | 819, | 323.9 | 712, | 317.2 | 809, | 357.1 | 708, | 349.5 |
| 810, | 307.5 | 711, | 301.4 | 819, | 324.0 | 705, | 315.8 | 801, | 356.8 | 701, | 349.3 |
| 808, | 306.7 | 705, | 300.5 | 807, | 323.8 | 705, | 315.8 | 799, | 356.4 | 699, | 349.3 |
| 800, | 307.0 | 702, | 300.8 | 800, | 322.8 | 702, | 316.6 | 790, | 355.9 | 690, | 345.2 |
| 798, | 306.9 | 690, | 300.0 | 789, | 321.8 | 692, | 315.9 | 785, | 355.3 | 598, | 341.3 |
| 790, | 306.4 | 685, | 297.5 | 788, | 322.1 | 680, | 315.0 | 780, | 355.1 | 581, | 337.0 |
| 781, | 305.1 | 627, | 294.8 | 779, | 321.3 | 641, | 312.2 | 770, | 354.6 | 560, | 332.0 |
| 780, | 305.8 | 612, | 294.5 | 778, | 321.4 | 609, | 309.3 | 760, | 353.7 | 463, | 327.5 |
| 778, | 304.9 | 587, | 292.0 | 772, | 320.9 | 602, | 309.5 | 750, | 353.3 | 404, | 321.9 |
| 770, | 305.0 | 582, | 292.3 | 770, | 320.9 | 562, | 306.3 | 755, | 353.5 | 367, | 316.0 |
| 766, | 304.8 | 548, | 269.0 | 766, | 320.7 | 519, | 302.5 | 750, | 353.0 | 310, | 309.5 |
| 759, | 304.3 | 544, | 289.4 | 760, | 320.3 | 485, | 298.5 | 745, | 352.7 | 270, | 303.7 |
| 757, | 303.9 | 530, | 287.9 | 758, | 319.8 | 447, | 296.0 | 743, | 352.5 | 232, | 297.5 |
| 751, | 303.6 | 505, | 286.1 | 755, | 320.0 | 410, | 290.7 | 740, | 352.2 | | |
| | | | | 753, | 319.8 | 409, | 292.0 | | | | |
| | | | | 750, | 319.5 | 370, | 287.5 | | | | |
| | | | | 749, | 319.6 | 331, | 288.0 | | | | |
| | | | | 740, | 319.0 | 252, | 271.5 | | | | |
| | | | | 733, | 318.3 | 225, | 264.0 | | | | |

A calculation of the value of heat of vaporization divided by absolute temperature from the above data was undertaken, since this was thought to be expected to throw some light on the question as to how far these compounds partake of the nature of fused salts. The values of Q/T for fused salts ought to be unusually high in view of the high degree of association which is usually attributed to them on other grounds (Bottomley, *Trans.*, 1903, 83, 1421; Lorenz and Kauffer, *Ber.*, 1908, 41, 3727). The vapour-pressure curve was first investigated by Ramsay and Young's method. The absolute temperatures at which the compounds attain certain vapour pressures are tabulated below, and compared with the corresponding temperature for a standard liquid (fluorobenzene):

TABLE I.

| P. | I. (THgCl_2). | II. $T(\text{HgBr}_2)$. | III. $T(\text{HgI}_2)$. | IV. $\text{TC}_6\text{H}_5\text{F}$. | I./IV. | II./IV. | III./IV. |
|-----|-----------------------------|-----------------------------|-----------------------------|--|--------|---------|----------|
| 240 | | 542.0 | 572.0 | 325.5 | | 1.665 | 1.757 |
| 300 | | 561.5 | 581.5 | 331.5 | | 1.662 | 1.756 |
| 580 | 561.0 | 576.5 | 608.5 | 347.0 | 1.617 | 1.662 | 1.754 |
| 790 | 578.0 | 589.0 | 622.5 | 358.0 | 1.810 | 1.655 | 1.749 |
| 800 | 579.5 | 596.0 | 629.5 | 360.5 | 1.608 | 1.653 | 1.747 |
| 860 | 583.0 | 599.5 | 633.5 | 363.0 | 1.606 | 1.651 | 1.746 |
| 900 | | 601.5 | 636.0 | 364.0 | | 1.650 | 1.745 |

From the above results a value of the constant was obtained in the equation:

$$\frac{T_A}{T_B} = \frac{T_A}{T_B} + c(T_B - T_B),$$

in which T_A are the temperatures of mercury halides, and T_B those of fluorobenzene at the same pressures.

$$c \text{ " for } \text{HgCl}_2 = 0.00050.$$

$$c \text{ " " } \text{HgBr}_2 = 0.00037.$$

$$c \text{ " " } \text{HgI}_2 = 0.00025.$$

The values of dP/dT were then found by a graphical method at a series of temperatures as tabulated below, and from these the heat of vaporisation Q and Q/T from the formula:

$$Q = \frac{1.985 T}{760} \left(T \frac{dP}{dT} \right) \text{ calories.}$$

Q and Q/T at 760 mm.

| | $Q(\text{cal.})$ | Q/T |
|-----------------------|------------------|-------|
| HgCl_2 | 13910 | 24.1 |
| HgBr_2 | 14200 | 23.8 |
| HgI_2 | 14700 | 23.5 |

It has been shown by Nernst that the normal value of Q/T at

760 mm. increases slightly with the boiling point of the liquid in question according to the formula:

$$Q/T = 9.5 \log T - 0.007T,$$

and for a liquid boiling at 304—354°:

$$Q/T = 22.19 \text{ normally.}$$

There appears, then, to be a certain amount of association, less, however, than in the case of water and alcohols, for which $Q/T = 26$. The association evidently diminishes in the order:



Specific Gravities of the Liquids.

Procedure.—After the right weight (10—15 grams) had been introduced into the dilatometer, this was evacuated, sealed, and after a preliminary heating (great care is necessary to avoid bursting the dilatometer) introduced into one of the thermostats and kept at each temperature until the volume remained constant.

After the experiments were completed, the dilatometers were opened and the contents boiled out, the weight of substance being thus checked. In calculating the volumes corresponding with each scale division of the dilatometers, the expansion of the silica was not taken into account, since it proved to be outside the range of accuracy aimed at.

Thus the greatest range of temperatures was from 255° to 357°. The linear expansion of silica is:

$$0.449 \times 10^{-6} \text{ or } 0.59 \times 10^{-6}.$$

Taking the larger figure, $3\alpha = 1.8 \times 10^{-6}$, and the total expansion of unit volume contained by a silica bulb at room temperature is 4.59×10^{-6} at 255°, and 6.43×10^{-6} at 357°.

The measured volumes have therefore to be increased, and the specific gravities decreased by about 1 in 2000.

This small correction has no effect on the relative specific volumes, but has been introduced into the absolute molecular volumes. The following specific gravities are calculated directly from the experimental data, the numbers to the left referring to different series of experiments in different thermostats with different quantities of compound and different thermometers.

Mercuric Chloride.

| <i>t</i> . | <i>D.</i> | <i>t</i> . | <i>D.</i> | <i>t</i> . | <i>D.</i> |
|------------|-----------|------------|-----------|------------|-----------|
| (1) 281.0 | 4.398 | (3) 290.7 | 4.377 | (5) 311.0 | 4.332 |
| (2) 287.7 | 4.376 | 301.6 | 4.357 | 318.0 | 4.316 |
| 290.7 | 4.369 | 304.6 | 4.348 | 328.0 | 4.298 |
| 300.6 | 4.348 | (4) 291.0 | 4.377 | 336.0 | 4.276 |
| | | 301.5 | 4.357 | (6) 357.0 | 4.238 |

Mercuric Bromide.

| | | | | | |
|-----------|-------|-----------|-------|-----------|-------|
| (1) 240.0 | 5.112 | (3) 253.0 | 5.066 | (4) 302.0 | 4.908 |
| 244.0 | 5.110 | 258.0 | 5.052 | (5) 253.5 | 5.054 |
| 251.0 | 5.078 | 260.0 | 5.044 | 280.5 | 4.976 |
| 261.5 | 5.046 | (4) 254.5 | 5.062 | 292.0 | 4.944 |
| (2) 241.5 | 5.104 | 260.0 | 5.044 | 301.5 | 5.054 |
| 248.0 | 5.082 | 272.0 | 5.007 | (6) 313.0 | 4.874 |
| 252.0 | 5.071 | 278.0 | 4.990 | 320.0 | 4.844 |
| 259.0 | 5.048 | 286.5 | 4.964 | 329.5 | 4.811 |
| (3) 250.0 | 5.076 | 293.5 | 4.938 | 339.0 | 4.784 |

Mercuric Iodide.

| | | | | | |
|-----------|-------|-----------|-------|-----------|-------|
| (1) 254.5 | 5.236 | (2) 281.0 | 5.160 | (4) 294.5 | 5.119 |
| 260.5 | 5.218 | (3) 275.0 | 5.177 | 301.5 | 5.090 |
| 266.0 | 5.207 | 279.0 | 5.166 | (5) 311.5 | 5.075 |
| 270.0 | 5.190 | 283.0 | 5.154 | 323.0 | 5.039 |
| 276.0 | 5.169 | 286.0 | 5.141 | 329.5 | 5.014 |
| 281.0 | 5.157 | 292.0 | 5.125 | 337.5 | 4.985 |
| (2) 259.5 | 5.226 | 294.5 | 5.113 | 339.0 | 4.978 |
| 267.5 | 5.208 | 301.5 | 5.090 | (6) 339.0 | 4.967 |
| 275.0 | 5.177 | (4) 282.5 | 5.154 | (7) 359.0 | 4.915 |

The alteration of density with temperature can be expressed as follows:

Mercuric Chloride, 280—335°:

$$D_t = 4.400 - 0.002218(t^\circ - 280).$$

Mercuric Bromide, 240—340°:

$$D_t = 5.116 - 0.00338(t^\circ - 240).$$

Mercuric Iodide, 255—355°:

$$D_t = 5.238 - 0.00322(t^\circ - 255).$$

Densities and Vapour Pressures of the Elements Compared with those of Compounds.

The data taken from the tables require no comment.

The densities of liquid iodine are those of Billet from *Constants of Nature* (Smithsonian). They appear somewhat irregular, which is due probably to the dark colour of the vapour at the higher temperatures. Special weight has been given to the values at the lower temperatures, and that found at the boiling point by Drugman and Ramsay (Trans., 1900, 77, 1228). The column

headed "pressure" refers as throughout to that of the saturated vapour:

TABLE II.

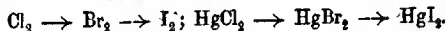
Density.

| Pressure. | Cl ₂ | Br ₂ | I ₂ | Hg | HgCl ₂ | HgBr ₂ | HgI ₂ |
|-----------|-----------------|-----------------|----------------|--------|-------------------|-------------------|------------------|
| 200 | 1.617 | 3.109 | 3.888 | 12.901 | | 5.037 | 5.134 |
| 400 | 1.535 | 3.050 | 3.795 | 12.824 | | 4.944 | 5.028 |
| 560 | 1.572 | 3.018 | 3.749 | 12.785 | 4.880 | 4.890 | 4.978 |
| 760 | 1.558 | 2.985 | 3.705 | 12.747 | 4.848 | 4.840 | 4.930 |
| 860 | 1.550 | 2.975 | 3.685 | 12.738 | 4.830 | 4.821 | 4.900 |

The expansions over certain intervals of pressure are compared with the normal below. Since the volumes are accurate to 0.2 per cent., the expansion, for example, between 560 and 860 mm. of mercury is 0.010 ± 0.002 in the case of mercuric chloride, and this is distinctly below the normal value. Thus for the pressure interval named, the value of the ratio $D(560)/D(860)$ is: Normal 1.023, Hg 1.003, Cl₂ 1.014, Br₂ 1.014, I₂ 1.017, HgCl₂ 1.010, HgBr₂ 1.014, HgI₂ 1.014.

The cause of these abnormalities is probably association as affecting not so much the liquid volumes as the vapour pressures, and hence the temperatures of comparison [see van't Hoff, *Lectures*, III, p. 27 (Lehfeldt)].

From the numerical values of the expansion the degree of association would appear to diminish in the order:



Now, comparing the expansions of the compounds with those of their constituent elements, it may be seen that the magnitude of the abnormality is such as would be produced if the expansion were additively composed of the expansions of the elements:

| Thus the ratios | | $\frac{V_M(860)}{V_M(560)}$ | and | $\frac{\Sigma V_A(860)}{\Sigma V_A(560)}$ |
|-----------------|--------------------------------------|-----------------------------|-----|---|
| are, for | HgCl ₂ and Hg + 2Cl | 1.010 | and | 1.012 |
| | HgBr ₂ ,, Hg + 2Br | 1.014 | ,, | 1.012 |
| | HgI ₂ ,, Hg + 2I | 1.014 | ,, | 1.015 |

While the magnitude of the possible volume error (14–20 per cent. on the expansion) does not permit of a certain conclusion on this point, yet the evidence for such a relation is strengthened by an examination of the few other compounds for which data are available.

Thus, comparing the ratios V_M and ΣV_A at 760 and 200 mm.:

| | | | |
|------------------------|-------|---------------|-------|
| PCl ₃ | 1.050 | P + 3Cl | 1.050 |
| ICl | 1.041 | I + Cl | 1.043 |

The importance of this for the question in hand rests in the

increased sensitivity it gives to the ratio $V_M/2V$ under various pressures.

In the first part of the paper reasons were given why the ratio should be quite constant in the case of normal elements and compounds far enough removed from their critical points.

It now appears that a constant ratio $V_M/2V_A$ can also be defined for the abnormally expanding elements and compounds considered, as may be seen from table III.

The variations of the ratios are within the limits of error to be expected from at least one of the volume measurements involved.

TABLE III
100 Volumes of the Elements before on Combination

| | <i>P</i> =360 mm. | 760 | 560 | |
|------------------------------------|-------------------|-------|-------|-------|
| HgCl ₂ , Hg + 2Cl | 101.9 | 101.8 | 101.7 | — |
| HgBr ₂ | 107.5 | 107.4 | 107.3 | — |
| HgI ₂ | 109.5 | 109.5 | 109.6 | — |
| | <i>P</i> =760 mm. | 560 | 400 | 200 |
| PCl ₅ → P + 3Cl | 105.6 | 105.2 | 104.9 | 105.0 |
| PBr ₅ | 107.8 | — | — | 107.5 |
| PI ₅ | 98.5 | — | — | — |
| PBr ₃ | 101.9 | — | — | 101.6 |

NOTE.—The vapour pressures and atomic volumes of the phosphorus halides and iodine chloride (referred to on p. 2042) are taken from the tables and Trans., 1907, 91, 1711; 1908, 95, 445. The temperature corresponding with 200 mm. for phosphorus tribromide has been calculated by Ramsay and Young's method (comparison liquid, phosphorus trichloride).

The expansion on combination therefore increases with increasing atomic weight for the mercuric halides as for the other compounds quoted (except phosphorus pentachloride, in which case the contraction on combination diminishes). According to the first part of this paper, the changes of volume on combination are approximately equal to the difference between the sums of the interatomic volumes of elementary molecules and the interatomic volume of the compound molecule. If this is correct the physical interpretation to be put upon the results is that, for example, the interatomic volume of a Cl₂ molecule is less than that of HgCl₂ (Hg being monatomic), and that in the other cases (except PCl₅) the sums of the interatomic volumes of the elementary molecules are less than the interatomic volume of the compound molecule. Now, comparing together two similar combinations, such as mercuric chloride and bromide, the relative increase of interatomic volume on combination is greater in the latter case, indicating a smaller molecular attraction for the atoms of mercuric bromide than for those of mercuric chloride. In the case of phosphorus halides, also,

the bromide combination exhibits a smaller molecular attraction as judged by these volume relations than the chloride. Thus the relative affinities are in the few cases investigated in the same order as the same affinities deduced from other considerations.

I desire to express my thanks to the Royal Society for a grant in aid of this research, and to Professor Donnan for the facilities afforded at the Muspratt Laboratory and the interest he has taken in the work.

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CCXIV.—Contributions to our Knowledge of the Sulphide Dyestuffs. Part I.

By GEORGE HERBERT FRANK.

SINCE the introduction of Vidal black (by R. Vidal, of Paris, in 1893), which, as is well known, is prepared by fusing together *p*-aminophenol (or *p*-aminophenol and other compounds) with sodium polysulphide, a large number of these so-called "sulphide" dyestuffs have been produced in a similar manner from aromatic compounds of varied constitution. The application of these colouring matters, especially to cotton, is of so simple a character, and the colours obtained are of so permanent a nature, that these compounds now constitute one of the most important groups of artificial dyestuffs. Although considerable insight has been gained as to the reactions occurring in their formation (Vidal, *Mon. Sci.*, 1903, [iv], 17, i, 427; Pollak, *Zeitsch. Farb. Ind.*, 1904, 3, 233, 253; Gnehm and Kaufler, *Ber.*, 1904, 37, 2617, 3032), the subject is beset by considerable difficulty, for the dyestuffs are as a rule amorphous, of a comparatively insoluble nature, do not yield well-characterised derivatives, and are accordingly not easily isolated in a pure condition.

During some experiments on the subject it was discovered that the leuco-compounds of many sulphide dyestuffs react with chloroacetic acid, and that the substances thus obtained, when oxidised, yield interesting colouring matters, differing considerably in properties from the parent substance. These new carboxyl derivatives are readily soluble in alkalis, pyridine or phenol, moderately so in boiling alcohol or acetic acid, but insoluble in dilute acids. They are well-defined colouring matters, giving shades similar to those

produced by the original sulphide dyes, and can be readily dyed on wool, but differ from the parent sulphide dyes in that they have very little affinity for cotton.

Among other points of interest attached to these substances it seemed possible that their closer examination would yield an insight as to the true molecular weight of the sulphide dyestuffs from which they were obtained, a point which would be of considerable help in regard to the vexed question of their constitution.

The following investigation deals with the well-known colouring matter, immedial-indone, which is manufactured by heating together *p*-aminophenol and *o*-toluidine with an aqueous solution of sodium sulphide. In order to purify the commercial product, it was repeatedly washed with warm water, treated with dilute hydrochloric acid until the liquor was faintly acid, and well washed. Fifty grams of the finely powdered product were reduced with sodium hydroxide and dextrose at 60–70° in the usual manner, and treated with 20 grams of a solution of sodium chloroacetate. An increase in temperature took place, and after fifteen minutes air was aspirated through the liquid in order to oxidise the leuco-compound. The liquid was now neutralised with dilute hydrochloric acid, the precipitated dye collected, extracted with warm sodium carbonate solution, the extract acidified, and the dye collected and dried; the product was now extracted with warm aniline, filtered from a slight residue, the solution neutralised with acid, and the precipitate again extracted with dilute sodium carbonate solution and acidified. As molecular-weight determinations in pyridine and nitrogen and sulphur estimations indicated that this product was not quite pure, it was submitted to a further treatment with warm aniline and extraction with dilute aqueous sodium carbonate in the manner above described, and finally dried in a vacuum desiccator. The compound obtained in this way contained no ash, and experiments indicated that it was now pure. It was of a deep blue, bronzy colour, readily soluble to a blue solution in aniline, pyridine, phenol, alkalis, or concentrated sulphuric acid, and sparingly so in hot glacial acetic acid or hot alcohol. Experiment indicated the absence of an amino-group, and, unlike the original immedial-indone, it had no affinity for cotton when dyed in a sodium sulphide bath, neither had its sodium salt any affinity for cotton, but the latter could be dyed on wool in the manner of an acid colour, giving a bright blue colour.

After being dried at 98°, it was analysed:

0.1241 gave 0.2494 CO₂ and 0.0459 H₂O. C=54.8; H=4.11.

0.2800 „ 17.3 c.c. N₂ at 13° and 757.7 mm. N=7.40,

0.1121 „ 0.1376 BaSO₄. S=16.88,

0.1312 gave 0.1559 BaSO_4 , $\text{S}=16.72$.

$\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{C}=54.4$; $\text{H}=4.0$; $\text{S}=17.07$;
 $\text{N}=7.48$ per cent.

0.5 Gram of the substance was treated with 10 c.c. of *N*-sodium hydroxide, and the solution was made up to 500 c.c.; by titration with *N*/10-hydrochloric acid and employing phenolphthalein as indicator, the acidity of the compound was first determined, and the neutral liquid thus produced was then treated with sodium tartrate and reduced with standard titanium chloride:

Found, $\text{NaOH}=21.12$ per cent. of the weight of the dye.

" $\text{H}_2=0.529$ " " " "
 $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{NaOH}=21.39$; $\text{H}_2=0.5347$ per cent.

Hence 189.9 parts of the colouring matter neutralise 40 parts of sodium hydroxide, and for the reduction of 378.2 parts, 2 parts of hydrogen are required.

A determination of the molecular weight was carried out by the cryoscopic method:

0.0854, in 10.3 of phenol, gave $\Delta t = -0.14^\circ$. $\text{M.W.}=377.4$.

$\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{M.W.}=374$.

When fused with sodium hydroxide, the substance undergoes an interesting change, for not only is sulphur thus removed, but also the carboxyl groups are eliminated. A blue compound insoluble in water or alkalis is thus produced. When reduced, this yields a leuco-derivative, but, unlike the corresponding leuco-derivatives of the sulphide dyestuffs, possesses no affinity for cotton.

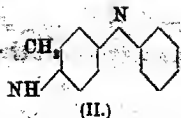
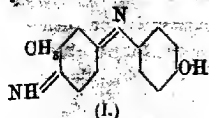
To obtain some further indication as to the nature of the reaction, quantitative experiment was carried out as follows:

0.5 Gram of the carboxyl derivative was fused at 200° with concentrated aqueous sodium hydrate until a colourless pasty mass, consisting of the leuco-compound of the new substance, was produced. The product when cold was diluted with water, the mixture neutralised with acid, and the colouring matter collected and washed. An estimation of the sulphur present gave the following result:

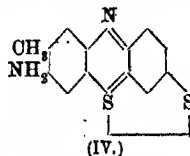
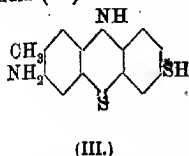
0.154 gave 0.1668 BaSO_4 . $\text{S}=14.89$ per cent.

Hence 215 parts of the substance contain 32 parts of sulphur. If from the found molecular weight of the carboxyl derivative we subtract $2(\text{CH}_2\text{CO}_2\text{H})+\text{S}=150$, the new substance should have a molecular weight of 227, which is in fair agreement with the above result. This experiment shows that one atom of sulphur can be removed from the molecule of the original carboxyl derivative, but that, on the other hand, the removal does not destroy the chromophoric group of this compound.

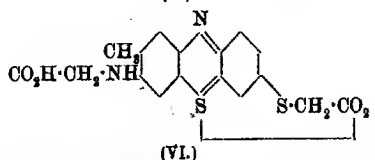
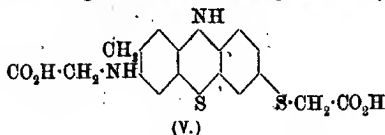
As immedial-indone is formed from the indophenol (I) obtained from *p*-aminophenol and *o*-toluidine, so the resultant dyestuff may be expected to possess the skeleton (II):



If we assume that, as is most probable during the reaction, sulphur enters in the *o*-position with respect to the nitrogen atom, and that the phenolic group is replaced by the thiol group, leuco-immedial-indone would have the constitution (III), and immedial-indone formula (IV):



Such a constitution would offer a ready explanation of the experiments given above. This compound would readily yield with chloroacetic acid a leuco-dicarboxylic derivative having the formula (V), and the colouring matter would be represented by (VI).



This investigation therefore indicates that the most probable constitution of immedial-indone is that given above; further experiments on this difficult subject are in progress.

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CCXV.—*The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change.*

By HARRY MEDFORTH DAWSON and ROBERT WHEATLEY, B.Sc.

IN a previous paper (Dawson and Leslie, *Trans.*, 1909, **95**, 1860) it has been shown that iodine reacts readily with acetone at the ordinary temperature, and that when aqueous solutions containing acetone and iodine are acidified by addition of a mineral acid, the reaction proceeds at a rate which is suitable for accurate quantitative measurements. These observations showed that when the acetone is present in considerable excess, the rate of disappearance of the iodine is practically constant from the commencement until near the end of the reaction, the velocity being proportional to the concentration of the acetone and of the added mineral acid.

To account for these facts, the view was adopted that the reaction between acetone and iodine involves two stages. In the first of these, the acetone is converted from the ketone into the enolic form, and this is then acted on by the iodine at a relatively very rapid rate with the formation of iodoacetone. In consequence of the very great difference in the velocities of the consecutive reactions, the rate of disappearance of the iodine is determined solely by the rate at which the acetone is transformed into the enolic form (compare Lapworth, *Trans.*, 1904, **85**, 30).

If this is the correct interpretation of the facts, it is evident that the investigation of the velocity of reaction of iodine with other ketones should lead to information respecting the rates at which the various ketones undergo tautomeric change. With this object in view, experiments were made to compare the rates of disappearance of iodine in dilute acidified solutions of dimethyl, methyl ethyl, methyl propyl, methyl butyl, methyl hexyl, phenyl methyl, diethyl, and phenyl ethyl ketones. On account of the small solubility of certain of these ketones in water, the comparative measurements could not be made in aqueous solution, and instead of this, an aqueous alcoholic solution containing forty volumes per cent. of ethyl alcohol was employed. In this connexion experiments were made to ascertain the influence of the medium on the reaction between acetone and iodine in alcohol-water mixtures ranging from pure water to pure alcohol. The results of this investigation will be communicated in a further paper. For the present it is sufficient to state that the reaction between the two substances is of the same character in alcoholic as in aqueous solution, and that, for a given concentration of acetone and acid, the rate of disappearance of iodine is practically the same in alcohol-water mixtures as it is

in pure water, if the amount of alcohol present does not exceed sixty to seventy volumes per cent. The only difference to be noted is the displacement of the final equilibrium as the ratio of the two components in the solvent is gradually altered. This influence of the medium is shown by the data in table I, which were obtained in parallel experiments with solutions containing 0, 20, 40, 60, 80, and 100 volumes per cent. of alcohol. The temperature at which these measurements were made was 25.1°.

TABLE I.

Initial iodine concentration = 0.0095; acetone = 0.272 *;
 $\text{H}_2\text{SO}_4 = 0.1$ mol. per litre.

| Volumes per cent. alcohol | 0 | 20 | 40 | 60 | 80 | 100 |
|---|----------|----------|---------|---------|---------|---------|
| Equilibrium iodine concentration ... | 0.000005 | 0.000015 | 0.00040 | 0.00100 | 0.00225 | 0.00442 |
| Percentage of un- changed iodine... | 0.05 | 0.15 | 4.2 | 10.5 | 23.7 | 48.5 |

* This concentration corresponds with 20 c.c. of acetone per litre.

These results show that the limit of the reaction is reached at a progressively earlier stage as the proportion of alcohol in the solvent increases, and the range of the velocity measurements is correspondingly diminished. In presence of potassium iodide, the reaction takes place still less completely. In the case of the first three solutions in the above table, the percentage of unchanged iodine was found to be 0.8, 2.3, and 16.9 respectively when potassium iodide was present to the extent of 0.02 mol. per litre. This effect of the iodide is no doubt due to the removal of iodine in consequence of the formation of polyiodides. In choosing a 40 per cent. alcoholic solution as the medium for the reacting substances, these circumstances were taken into consideration, and the alcohol-water mixture in question represents the smallest proportion of alcohol which is necessary for the solution of the majority of the ketones in the requisite concentration.

The limit of the reaction in the aqueous-alcoholic solution varies with the nature of the ketone. This is evident from a consideration of the data in table II, which gives the results obtained for acetone, diethyl ketone, and acetophenone. In these and all other experiments the relative concentrations of ketone and iodine were such that the active mass of the ketone could be regarded as constant during the course of the reaction. Similarly, the concentration of the sulphuric acid was so large that no appreciable alteration in its value resulted from the formation of the hydriodic acid during the reaction.

The ketone was weighed out into a graduated stoppered flask

containing water and measured quantities of alcohol and standard sulphuric acid solution. The flask was placed in a thermostat at 25.1° , and after some time a known quantity of iodine was added in the form of an aqueous potassium iodide solution, and the contents were made up to the mark with water. After definite time intervals, portions of the solutions were removed, added to excess of a sodium hydrogen carbonate solution, and titrated with a freshly prepared 0.01*N* solution of sodium thiosulphate.

In the following tables x_1 is the observed iodine concentration in mols. per litre, and x_2 the concentration calculated from the equation $x_2 = x_0 - kt$, in which x_0 is the first observed concentration ($t=0$), and k the velocity constant $= dx/dt$. The concentrations of the ketone and the acid and the original concentration of the iodine are given in every case in mols. per litre.

TABLE II.

*Acetone.*Acetone = 0.1886; $H_2SO_4 = 0.1$; iodine = 0.0101.

| Time (minutes) | 0 | 25 | 45 | 65 | 85 | 105 | 140 | 24 hours |
|------------------|--------|------|------|------|------|------|------|----------|
| $x_1 \cdot 10^4$ | 91.8 | 77.8 | 67.4 | 57.2 | 46.9 | 37.9 | 27.5 | 20.3 |
| $x_2 \cdot 10^4$ | (91.8) | 78.3 | 67.5 | 56.7 | 45.9 | 35.1 | 16.2 | — |

$$k = 0.000054.$$

*Diethyl Ketone.*Ketone = 0.2532; $H_2SO_4 = 0.1$; iodine = 0.0102.

| Time (minutes) | 0 | 30 | 60 | 80 | 105 | 120 | 135 | 24 hours |
|------------------|--------|------|------|------|------|------|------|----------|
| $x_1 \cdot 10^4$ | 90.4 | 72.7 | 54.7 | 43.0 | 28.5 | 20.4 | 12.9 | 2.2 |
| $x_2 \cdot 10^4$ | (90.4) | 72.7 | 55.0 | 43.2 | 28.4 | 19.6 | 10.8 | — |

$$k = 0.000059.$$

*Acetophenone.*Ketone = 0.1673; $H_2SO_4 = 0.1$; iodine = 0.0101.

| Time (minutes) | 0 | 15 | 51 | 75 | 105 | 135 | 165 | 255 | 24 hour |
|------------------|--------|------|------|------|------|------|------|------|---------|
| $x_1 \cdot 10^4$ | 98.3 | 95.6 | 89.2 | 84.8 | 79.3 | 74.5 | 70.2 | 57.7 | 42.4 |
| $x_2 \cdot 10^4$ | (98.3) | 95.6 | 89.1 | 84.8 | 79.4 | 74.0 | 68.6 | 52.4 | — |

$$k = 0.000018.$$

From a comparison of the equilibrium iodine concentrations recorded under $t=24$ hours, it is evident that the extent to which the reaction proceeds is dependent on the nature of the ketone in solution. Although the above three experiments are not strictly comparable because of the differences in the ketone concentrations, it is seen that in the acetone, diethyl ketone, and acetophenone solutions the unchanged iodine amounts to about 20, 2, and 40 per cent. respectively. Of the ketones examined, the reaction proceeds

furthest in the case of diethyl ketone, and to the smallest extent in the case of acetophenone, and on this account data are recorded for these two substances, as well as for acetone, which show the progress of the reaction throughout the greater part of its course.

On comparing the values of x_1 and x_2 , it is seen that in the case of acetone, the rate of disappearance of the iodine is constant until about 50 per cent. of the iodine originally present has reacted, and that the velocity then diminishes as the equilibrium condition is approached. For diethyl ketone the velocity remains constant until about 75 per cent. of the iodine has disappeared, whereas, in the case of acetophenone, the velocity shows distinct evidence of diminution when about 30 per cent. of the iodine has reacted. The point at which the velocity begins to fall is obviously determined by the proportion of the original iodine which remains when the condition of equilibrium has been reached. The more complete the reaction, the greater is the range over which the reaction velocity remains constant.

In the communication of further results this circumstance is taken into consideration, and the measured velocities relate solely to that part of the total reaction in which the iodine disappears at a constant rate. Table III contains the data obtained in experiments with other ketones, the calculated iodine concentrations being placed alongside the observed values, as in table II:

TABLE III.

Methyl Ethyl Ketone.

Ketone = 0.174; H_2SO_4 = 0.095 mol. per litre.

| | | | | | |
|------------------|--------|------|------|------|------|
| Time (minutes) | 0 | 30½ | 57½ | 85½ | 129 |
| $x_1 \cdot 10^4$ | 94.8 | 79.4 | 66.1 | 52.9 | 34.4 |
| $x_2 \cdot 10^4$ | (94.8) | 79.8 | 66.3 | 52.5 | 31.2 |

$$k = 0.0000495.$$

Methyl Propyl Ketone.

Ketone = 0.1727; H_2SO_4 = 0.1 mol. per litre.

| | | | | | |
|------------------|--------|------|------|------|------|
| Time (minutes) | 0 | 30 | 47 | 60 | 95 |
| $x_1 \cdot 10^4$ | 92.1 | 78.0 | 69.8 | 64.0 | 47.6 |
| $x_2 \cdot 10^4$ | (92.1) | 78.0 | 70.0 | 63.9 | 47.5 |

$$k = 0.0000453.$$

Methyl Butyl Ketone.

Ketone = 0.1678; H_2SO_4 = 0.1 mol. per litre.

| | | | | | |
|------------------|--------|------|------|------|------|
| Time (minutes) | 0 | 35 | 45 | 60 | 95 |
| $x_1 \cdot 10^4$ | 89.5 | 76.3 | 66.2 | 53.1 | 45.5 |
| $x_2 \cdot 10^4$ | (89.5) | 76.4 | 66.0 | 53.1 | 45.1 |

$$k = 0.0000523.$$

*Methyl Hexyl Ketone.*Ketone = 0.0814; H_2SO_4 = 0.1 mol. per litre.

| | | | | | |
|------------------|--------|------|------|------|------|
| Time (minutes) | 0 | 30 | 70 | 100 | 130 |
| $x_1 \cdot 10^4$ | 73.3 | 65.8 | 55.7 | 48.3 | 41.2 |
| $x_2 \cdot 10^4$ | (73.3) | 65.8 | 55.8 | 48.3 | 40.8 |

$$k = 0.000025.$$

*Phenyl Ethyl Ketone.*Ketone = 0.0855; H_2SO_4 = 0.251 mol. per litre.

| | | | | | | |
|------------------|--------|------|------|------|------|------|
| Time (minutes) | 0 | 120 | 235 | 350 | 430 | 565 |
| $x_1 \cdot 10^4$ | 96.6 | 90.0 | 83.6 | 78.3 | 71.8 | 67.4 |
| $x_2 \cdot 10^4$ | (96.6) | 90.4 | 84.4 | 78.4 | 71.6 | 67.2 |

$$k = 0.000052.$$

In addition to the above experiments others were made in which the concentrations of the various ketones and of the acid were approximately doubled or halved. These indicate that the various reactions take place at a rate which is proportional to the ketone and acid concentrations, as was found to be the case for the action between iodine and acetone in aqueous solution. Apart from the constancy of the reaction velocity, the fact that the influence of ketone and acid concentration is the same for all the ketones examined affords strong evidence in support of the view that the cause of the uniform speed of the reaction is the same in all cases, that is to say, a change in the ketone from the ketonic to the enolic form.

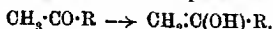
On the basis of the observed proportionality between the velocity and the ketone and acid concentrations, the several values obtained for the speed of the reactions may be reduced to a uniform ketone and acid concentration (ketone = 1/6 mol. per litre; sulphuric acid = 0.1 mol. per litre). In this way the velocities of reaction recorded in the second column of table IV are obtained. These numbers may be taken as representing the relative rates at which the ketonic forms of the various members of the series are converted into the corresponding enolic forms. The velocities with reference to acetone as standard are given in the third volume.

TABLE IV.

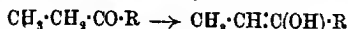
| Ketone. | k (mols. per litre per minute). | Relative k values. |
|----------------------------|-----------------------------------|----------------------|
| Acetone | 48×10^{-6} | 1 |
| Methyl ethyl ketone | 50×10^{-6} | 1.04 |
| Methyl propyl ketone | 45×10^{-6} | 0.94 |
| Methyl butyl ketone | 53×10^{-6} | 1.10 |
| Methyl hexyl ketone | 51×10^{-6} | 1.06 |
| Acetophenone | 18×10^{-6} | 0.37 |
| Diethyl ketone | 89.5×10^{-6} | 0.82 |
| Phenyl ethyl ketone | 4.0×10^{-6} | 0.083 |

From the above values of k , it is seen that the replacement of one of the methyl groups in acetone by ethyl, propyl, butyl, or hexyl does not cause very much alteration in the rate at which the substance reacts with iodine. On the other hand, the reactivity is reduced to nearly one-third when the methyl group is replaced by phenyl. For diethyl ketone the velocity is only about 20 per cent. smaller than in the case of acetone, and substitution of phenyl for one of the ethyl groups reduces the reactivity to about one-tenth.

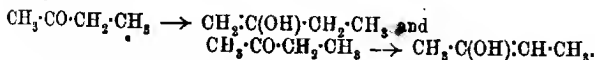
On the assumption that the measured velocities are determined by the respective rates of tautomeric change, it is not surprising that the first five ketones should be found to react with iodine at approximately the same rate, for in each case the transformation involved may be supposed to be that represented by



On the other hand, the fact that the reactivity of diethyl ketone is nearly as great as that of the methyl ketones would seem to show that the change represented by



may take place almost as readily as the previous one. That this approximate equality of the rates of change of the groups $\text{CH}_3\cdot\text{CO}\cdot$ and $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot$ is not general, however, is evident from a comparison of the values for acetophenone and phenyl ethyl ketone. As shown by experiments with benzophenone, the phenyl group does not react at all with iodine under the conditions of the dynamic experiments, and it might be expected that the ratio of the reactivities of these two substances would be the same as the ratio found in the case of acetone and diethyl ketone. This is not the case, the observed velocity of reaction in the case of acetophenone being about four and a-half times as great as that found for phenyl ethyl ketone. In other words, the relative rates at which the groups $\text{CH}_3\cdot\text{CO}\cdot$ and $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot$ undergo tautomeric change is dependent on the nature of the radicle with which the two groups are combined. On the other hand, the approximate equality of the rates of reaction of dimethyl and diethyl ketone with iodine leads us to anticipate that methyl ethyl ketone will react with iodine in two ways, which are determined respectively by the tautomeric changes:



The amounts of the corresponding iodo-substitution products will be conditioned by the relative rates at which these two changes take place. On the basis of the results which have been obtained with the aliphatic ketones, it appears probable that aliphatic ketones

will in general give rise to two substitution products for the velocities of the two possible tautomeric changes are apparently of the same order of magnitude.

Preliminary experiments have been made which show that certain aldehydes react with iodine in a similar manner to that observed for the various ketones investigated in this paper. This is the case for propaldehyde, whereas the kinetic investigation of the reaction between acetaldehyde and iodine indicates that the mechanism of this change is of a different kind. This question is being further investigated.

The chief results obtained in this inquiry are:

1. Evidence is adduced to show that the mechanism involved in the reaction of iodine on various ketones is of the same kind, the progress of the change being determined by the rate at which the enolic form of the ketone is formed.
2. From the measurement of the velocities with which the ketones react with iodine, the relative rates at which the ketones undergo tautomeric change have been obtained.

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CCXVI.—*The Constitution of Eriodictyol, of Homoeriodictyol, and of Hesperitin.*

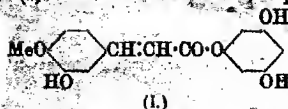
By FRANK TUTIN.

IN a paper communicated to the meeting of the American Pharmaceutical Association, held at Indianapolis, Ind., in September, 1906, Dr. F. B. Power and the present author described the isolation of two crystalline substances of phenolic nature from the leaves of *Eriodictyon Californicum* (Hooker and Arnott), Greene (*Proc. Amer. Pharm. Assoc.*, 1906, 54, 352). These two compounds were designated eriodictyol and homoeriodictyol respectively, the former having been proved to possess the formula $C_{15}H_{12}O_6$, whilst the composition of the latter was shown to be $C_{16}H_{14}O_6$.

In a subsequent communication (*Trans.*, 1907, 91, 887) it was noted that there are certain similarities in the properties of homoeriodictyol and its isomeride, hesperitin, which suggested that these two compounds were structurally related. Experiments supported this view, for, whilst hesperitin yields caffeic acid (3-hydroxy-4-methoxycinnamic acid) and phloroglucinol on hydrolysis (Tiemann and Will, *Ber.*, 1881, 14, 379), homoeriodictyol, when

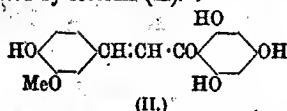
similarly treated, gave the same phenol together with ferulic acid (4-hydroxy-3-methoxycinnamic acid).

Tiemann and Will (*loc. cit.*) assigned to hesperitin the constitutional formula (I). This formula received support through the

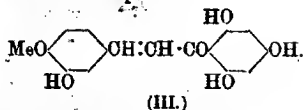


work of A. G. Perkin (Trans., 1898, 73, 1037), who prepared acetylhesperitin, and recorded results which indicated that this compound was a triacetyl derivative.

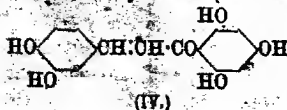
It appeared therefore from the results of the hydrolysis experiments mentioned above that homoeriodictyol differed from hesperitin only in the relative positions of the hydroxyl and methoxyl groups in the catechol part of the molecule. When, however, acetylhomoeriodictyol was prepared, it was found to contain four acetyl groups. It was therefore concluded that homoeriodictyol must be represented by formula (II).



From this it would appear that homoeriodictyol was not so similar to hesperitin in structure as had at first been concluded. Nevertheless, Dr. Power and the present author were so convinced of the near relationship of these two compounds that they ventured to suggest that the formula hitherto assigned to hesperitin is incorrect, notwithstanding the statement of Perkin (*loc. cit.*) that the latter yields only a triacetyl derivative. Formula (III) was therefore put forward for hesperitin.

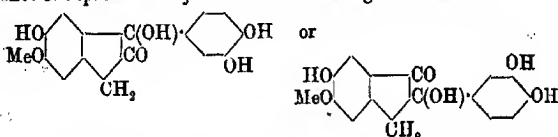


With regard to the constitution of eriodictyol, the amount of material which was at first available did not permit of many experiments being conducted with this substance, but the view was expressed that it was the parent compound of which hesperitin and homoeriodictyol are monomethyl ethers (formula IV).



Shortly after the appearance of the first paper by Power and Tutin on eriodictyon leaves (*loc. cit.*), a communication on the same subject was published by G. Mossler (*Annalen*, 1907, 351, 233). This author recorded the isolation of a substance possessing the formula $C_{16}H_{14}O_6$, designated "eriodictyonon," which was evidently identical with homoeriodictyol. Mossler, however, did not succeed in isolating any eriodictyol.

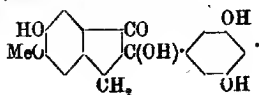
After having published the account of their work on the constitution of homoeriodictyol, Dr. Power and the present author received from Dr. Mossler a reprint of a paper communicated by him to the Academy of Sciences in Vienna (*Sitzungsber. K. Akad. Wiss. Wien*, 1907, 116, ii, June, 1907). In this communication Mossler, who was unaware of the more recent work of the above-mentioned authors, admits that his "eriodictyonon" is identical with homoeriodictyol, and sets forth the conclusion that this substance is represented by one of the following formulae:



This last publication by Mossler was replied to by Dr. Power and the present author (*Proc.*, 1907, 23, 243), when it was pointed out that neither of the formulae proposed by Mossler could be correct, since compounds possessing such a structure could not yield phloroglucinol.

One statement made by Mossler, however, was in direct conflict with the views which the present author, in conjunction with Dr. Power, had expressed regarding the constitution of homoeriodictyol, namely, that the substance in question was optically active. The last-mentioned authors were unable to confirm this, and, since the correctness of their conclusions regarding homoeriodictyol have now been fully proved, it is evident that the above statement of Mossler must have been based on an incorrect observation.

It appeared to the present author that there was one possible alternative to the formula which had been suggested by him in conjunction with Dr. Power for homoeriodictyol, but which was not at all probable, namely, a structure related to the second formula proposed by Mossler, as follows:



A substance possessing such a formula might conceivably yield, on hydrolysis, phloroglucinol and tartaric acid by the addition of two molecules of water, followed by the elimination of one such molecule, although such a change appeared highly improbable. It was considered advisable, therefore, in order conclusively to prove the constitution of homoeriodictyol and related compounds, to have recourse to synthetical experiments.

If the formulae suggested by Dr. Power and the present author for eriodictyol, homoeriodictyol, and hesperitin be correct, then these substances are 2:4:6-trihydroxyphenyl 3:4-dihydroxystyryl ketone, 2:4:6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone, and 2:4:6-trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone respectively. It was decided therefore to methylate the first-mentioned three substances, and to compare the fully methylated products with synthetically prepared 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone. The results of the methylation of eriodictyol, homoeriodictyol, and hesperitin are recorded in the present paper, and it is shown that each of them yields 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone and 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone identical in all respects with these substances as prepared synthetically (see the following paper).

The correctness of the formulae suggested by Power and Tutin for eriodictyol, homoeriodictyol, and hesperitin is therefore proved beyond question.

Naringenin, a hydrolytic product of the glucoside, naringin, was shown by Will (*Ber.*, 1885, 18, 1311) to be related to hesperitin. On heating with aqueous potassium hydroxide, it undergoes hydrolysis in a manner similar to the latter compound, and yields phloroglucinol and *p*-hydroxycinnamic acid. Will therefore concluded (*Ber.*, 1887, 20, 297) that naringenin was the phloroglucinyl ester of the above-mentioned acid. In view of the results recorded in the present paper concerning hesperitin, there can be no doubt that naringenin is also a ketone, namely, 2:4:6-trihydroxyphenyl 4-hydroxystyryl ketone.

In a previous communication (Power and Tutin, *Trans.*, *loc. cit.*) a monomethyl ether of homoeriodictyol was described. A larger quantity of this substance has now been prepared, and it has been proved to be 2:6-dihydroxy-4-methoxyphenyl 4-hydroxy-3-methoxystyryl ketone. Similarly, when one methyl group is introduced into eriodictyol, it takes up the 4-position in the phenyl radicle, the product being a new isomeric of homoeriodictyol and hesperitin, namely, 2:6-dihydroxy-4-methoxyphenyl 3:4-dihydroxystyryl ketone.

The observation of Perkin (*loc. cit.*) regarding the anomalous character of the sodium derivative of hesperitin has been confirmed, this substance appearing to have the formula $C_{18}H_{18}O_6Na, C_{18}H_{14}O_6$. On the other hand, the statement made by Perkin that the product of the action of acetic anhydride on hesperitin is a triacetyl derivative cannot be confirmed, it having been proved that the substance thus formed is *tetra-acetylhesperitin*.

EXPERIMENTAL

Eriodictyol (2:4:6-Trihydroxyphenyl 3:4-Dihydroxystyryl Ketone).

A quantity (5 grams) of eriodictyol* was dissolved in alcohol, and an excess of methyl sulphate† added, after which a concentrated alcoholic solution of potassium hydroxide was allowed to flow into the hot liquid at such a rate that the mixture was kept gently boiling. The liquid at first showed a tendency to darken, owing to the absorption of oxygen, but this soon ceased as methylation proceeded. Finally, the mixture assumed a dark red colour on the addition of the alkali, which only slowly disappeared. A further quantity of methyl sulphate was added, followed by more alkali, after which the mixture was kept for twenty minutes and then poured into water. The yellow product precipitated by this treatment was extracted by means of chloroform, the solution being washed, dried, and the solvent removed. The residue thus obtained was boiled with successive portions of dilute, aqueous potassium hydroxide so long as the decanted alkaline liquid was yellow in colour, after which the material insoluble in the alkali was washed and dissolved in alcohol. On inoculating the solution thus obtained with synthetic 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (see the following paper), crystallisation rapidly ensued. The product so obtained was identical in all respects with the synthetical compound just mentioned. It crystallised in stout, pale yellow prisms, and, when dried in the air, melted at 85° , but in the anhydrous state at 117.5° :

0.1747 † gave 0.4279 CO_2 and 0.1046 H_2O . C=66.8; H=6.4.

$C_{20}H_{22}O_6$ requires C=67.0; H=6.1 per cent.

The potassium hydroxide extracts which had been decanted from the crude 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone were acidified, and the precipitated yellow product was crystallised from alcohol, in which it was rather sparingly soluble. Deep yellow

* For an improved method of isolating eriodictyol, homoeriodictyol, and other phenolic substances from *Eriodictyon* leaves, compare Tutin and Clewer, *Trans.* 1909, 95, 81.

† Anhydrous substance.

leaflets were thus obtained, which melted at 154° , and were identical with the 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone described in the following paper:

0.1279 gave 0.3099 CO_2 and 0.0680 H_2O . $\text{C} = 66.1$; $\text{H} = 5.9$.

$\text{C}_{19}\text{H}_{20}\text{O}_6$ requires $\text{C} = 66.3$; $\text{H} = 5.8$ per cent.

Monomethyleriodictyol (2:6-Dihydroxy-4-methoxyphenyl 3:4-dihydroxystyryl ketone).—Four grams of eriodictyol were dissolved in absolute alcohol, and to this solution was added one and a-half molecular proportions of methyl sulphate, which had just previously been washed with aqueous sodium carbonate and dried. Slightly more than the equivalent amount of sodium, dissolved in absolute alcohol, was then gradually introduced into the hot mixture. After removing the alcohol, the residue was dissolved in ether, washed with water, and then fractionally extracted by shaking with successive portions of an aqueous solution of sodium carbonate. The first few extractions removed only unchanged eriodictyol, which formed the greater part of the product, but on acidifying the alkaline liquids subsequently obtained, a yellow product separated, which partly crystallised on keeping. This was collected, well washed with alcohol, and then recrystallised from this solvent, in which it was but sparingly soluble. Almost colourless needles were thus obtained, which melted at 215° :

0.1284 gave 0.2995 CO_2 and 0.0583 H_2O . $\text{C} = 63.6$; $\text{H} = 5.0$.

$\text{C}_{18}\text{H}_{14}\text{O}_6$ requires $\text{C} = 63.5$; $\text{H} = 4.6$ per cent.

This substance was therefore a *monomethyleriodictyol*, and since it is not identical with either homoeriodictyol (2:4:6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone) or hesperitin (2:4:6-trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone), and the hydroxyl group in the 2(or 6)-position is known to be difficult of methylation, it must be 2:6-dihydroxy-4-methoxyphenyl 3:4-dihydroxystyryl ketone.

Monomethyleriodictyol dissolves in aqueous alkali hydroxides, giving at first a practically colourless solution, but after about thirty seconds the liquid suddenly becomes totally black. On acetylation, monomethyleriodictyol yields a *tetra-acetyl* derivative, which forms colourless needles, melting at 159° .

Homoeriodictyol (2:4:6-Trihydroxyphenyl 4-Hydroxy-3-methoxystyryl Ketone).

The methylation of homoeriodictyol by means of methyl sulphate and potassium hydroxide proceeded analogously to that of eriodictyol, with the exception that there was no tendency to absorb oxygen, and consequently a cleaner product was obtained. The

metanoylated material was examined as above described, when it readily yielded 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 85° when air-dried; 117.6° when anhydrous) and 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 154°).

Monomethylhomoeriodictyol (2:6-Dihydroxy-4-methoxyphenyl 4-hydroxy-3-methoxystyryl ketone). — Monomethylhomoeriodictyol, prepared by the action of methyl iodide on the crystalline sodium derivative of homoeriodictyol, was previously described by Power and Tutin (*Trans.*, 1907, **91**, 895). A larger amount of this product has now been prepared by heating the above-mentioned sodium derivative with methyl iodide and methyl alcohol. The product thus obtained was dissolved in ether and freed from unchanged homoeriodictyol by extraction with dilute, aqueous sodium carbonate, after which the monomethylhomoeriodictyol was removed by shaking with a concentrated solution of this alkali. The product so obtained crystallised readily from alcohol in hard, yellow, wart-like masses, which melted at 142° .

On boiling monomethylhomoeriodictyol for several hours with 30 per cent. aqueous potassium hydroxide, hydrolysis occurred at the double linking, after which vanillin was readily isolated from the reaction mixture. It is evident from this, and considerations previously given, that the ONa group in the sodium derivative of homoeriodictyol, which is converted into methoxyl on treatment with methyl iodide, must occupy the 4-position in the phenyl group of the molecule. Monomethylhomoeriodictyol is therefore 2:6-dihydroxy-4-methoxyphenyl 4-hydroxy-3-methoxystyryl ketone.

Hesperitin (2:4:6-Trihydroxyphenyl 3-Hydroxy-4-methoxystyryl Ketone.)

Hesperitin, which is obtained by the hydrolysis of the glucoside, hesperidin, a constituent of the peel of the orange, lemon, and other related fruits, has been stated by Tiemann and Will (*Ber.*, 1881, **14**, 970) to be the phloroglucinyl ester of isoferulic acid. As stated in the introductory portion of this paper, however, the accuracy of this conclusion was doubted by Power and Tutin, and the present author has therefore further investigated the question.

Hesperitin, as obtained from Schuchardt, was recrystallised from ethyl acetate, when it melted at 224° , but when mixed with homoeriodictyol, fusion occurred at 200° . The material so obtained, however, did not agree in its characters with the description of hesperitin as given by A. G. Perkin (*Trans.*, 1896, **73**, 1037). Thus it formed pale yellow plates, which could not be distinguished

by inspection from crystals of homoeriodictyol, it was practically tasteless* and dissolved in alkalis with a bright yellow colour. Perkin (*loc. cit.*) on the other hand, has described hesperitin as crystallising in colourless needles, possessing an intensely sweet taste and dissolving in alkalis with, at the most, a faintly yellow colour. Nevertheless, the identity of the material employed by the present author with hesperitin cannot be doubted, inasmuch as the melting point of the compound itself and its acetyl derivative are in agreement with the corresponding constants given by Perkin for hesperitin and its acetyl derivative. Moreover, the substance yielded the abnormal sodium derivative, $C_{16}H_{13}O_6Na.C_{10}H_{14}O_6$, characteristic of hesperitin. (Found, Na=3.8. Calc., Na=3.8 per cent.)

Methylation of Hesperitin.

A quantity (1.5 grams) of hesperitin was methylated by means of potassium hydroxide and methyl sulphate in the manner previously described, when the reaction appeared to proceed precisely as in the case of homoeriodictyol. A good yield of product was obtained, which was readily separated into the two compounds similarly prepared from eriodictyol and its homologue, namely, 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 154°) and 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 85° when air-dried; 117.5° when anhydrous).

Tetra-acetylhesperitin.—Half a gram of hesperitin was boiled for three hours with a considerable excess of acetic anhydride, after which the greater part of the solvent was removed and the mixture diluted with ether. After several hours, a crystalline substance separated in tufts of colourless prisms, which melted at 120°. After recrystallisation from alcohol, this substance melted at 127°, and was evidently identical with the compound similarly prepared by Perkin (*loc. cit.*), which he regarded as a triacetyl derivative. The number of acetyl groups in the compound were estimated as follows. A quantity of the substance was hydrolysed with dilute potassium hydroxide, the mixture then acidified with sulphuric acid, and the acetic acid removed by a current of steam and titrated:

0.2616 gave acetic acid equivalent to 0.0900 NaOH. $CO \cdot CH_3 = 36.9$.
 $C_{16}H_{13}O_6(OO \cdot CH_3)_4$ requires $CO \cdot CH_3 = 36.6$ per cent.

It is evident therefore that this compound was *tetra-acetylhesperitin*, and not a triacetyl derivative. This conclusion is in harmony with the properties of the substance, for it was insoluble

* Although hesperitin, when in the solid state, possesses no appreciable taste, its alcoholic solution is distinctly sweet.

in cold dilute sodium hydroxide, which would not have been the case had it contained a hydroxyl group, all the groups of this nature present in hesperitin having phenolic properties.

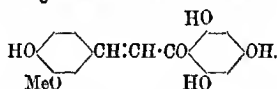
THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXVII.—*The Synthesis of 2:4:6-Trimethoxyphenyl 3:4-Dimethoxystyryl Ketone. A Methyl Derivative of Eriodictyol, Homoeriodictyol, and Hesperitin.*

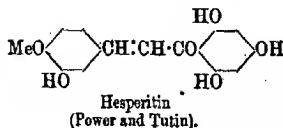
By FRANK TUTIN and FREDERIC WILLIAM CATON.

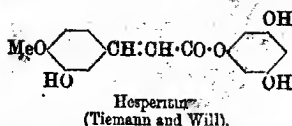
SOME time ago Power and Tutin (*Proc. Amer. Pharm. Assoc.*, 1906, 54, 352) isolated from the leaves of *Eriodictyon Californicum* (Hooker and Arnott), Greene, two crystalline substances of phenolic nature, which were designated eriodictyol and homoeriodictyol respectively. Eriodictyol was shown to possess the formula $C_{15}H_{12}O_6$, whilst homoeriodictyol was found to be isomeric with hesperitin, having the formula $C_{16}H_{14}O_6$.

In a subsequent communication (Power and Tutin, *Trans.*, 1907, 91, 887) results were recorded which indicated that homoeriodictyol possesses the following constitutional formula:



The amount of eriodictyol at that time available did not permit of many experiments being conducted with this substance, but the conclusion was drawn that it differed from its homologue only by having a hydroxyl in the place of the methoxyl group. It was furthermore suggested from certain similarities in the properties of homoeriodictyol and hesperitin that these two substances differed only in the relative positions of the hydroxyl and methoxyl groups in the catechol part of the molecule, and that, consequently, the constitutional formula hitherto assigned to hesperitin was incorrect (Tiemann and Will, *Ber.*, 1881, 14, 970; Perkin, *Trans.*, 1898, 73, 1037):

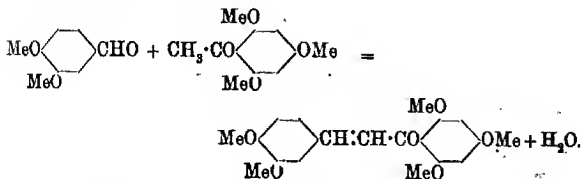




The above conclusions have now all been confirmed, inasmuch as, in the preceding paper, it is shown that eriodictyol, homoeriodictyol, and hesperitin each yield the same product when fully methylated. Final and conclusive proof of the structure of these compounds was, however, desirable, and it appeared that this could best be obtained by the synthesis of the fully methylated product.

If the views previously expressed regarding the constitution of eriodictyol, homoeriodictyol, and hesperitin be correct (Power and Tutin, *Trans. loc. cit.*), then these substances are 2:4:6-trihydroxyphenyl 3:4-dihydroxystyryl ketone, 2:4:6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone, and 2:4:6-trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone respectively. It was therefore sought to synthesize 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone in order that it might be compared with the compound obtained on fully methylating the naturally occurring substances under consideration. This has been accomplished, and the synthetic compound has been found to be in all respects identical with the product obtained from the three substances occurring in nature, thus affording conclusive proof of the constitution of the latter compounds.

2:4:6-Trimethoxyacetophenone was prepared by the interaction of acetyl chloride and phloroglucinol trimethyl ether in the presence of anhydrous ferric chloride, and this ketone was condensed with vanillin methyl ether by means of "molecular" sodium in a manner similar to that employed by Perkin and Weizmann (*Trans.*, 1906, 89, 1649), when 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone resulted in good yield:



This substance gave, on heating with aluminium chloride, a hydroxytetramethoxy-compound, which melted at practically the same temperature as 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone described by Kostanecki (*Ber.*, 1904, 37, 793).

The present authors, however, were unable to obtain from the substance prepared by them the acetyl derivative described by Kostanecki. Nevertheless it is considered certain that the trimethyl tetramethoxy compound obtained by the present authors is identical with that prepared by Kostanecki, inasmuch as the latter author has shown that a methoxyl group in the phloroglucinol nucleus situated in the 2-position with respect to the side chain is not easily hydrolysed by aluminium chloride.

2:4:6-Trimethoxyacetophenone was prepared by Kostanecki (*Ber.*, 1899, 32, 2262) in the manner already mentioned, but it has previously been stated by Friedländer and Schnell (*Ber.*, 1897, 30, 2150) to result from the interaction of phloroglucinol trimethyl ether and acetyl chloride in the presence of aluminium chloride. The present authors, however, could succeed in preparing it only by Kostanecki's method, and, when employing that of the earlier investigators, obtained a *hydroxydiacetyldimethoxybenzene*, $C_{12}H_{14}O_6$.

EXPERIMENTAL

Methylation of Phloroglucinol.

Will (*Ber.*, 1888, 21, 603) obtained phloroglucinol trimethyl ether by the action of sodium and methyl iodide on the dimethyl ether, the latter being prepared by passing anhydrous hydrogen chloride into a methyl-alcoholic solution of phloroglucinol. The present authors, with the endeavour to simplify this process, sought to obtain the trimethyl ether by the direct methylation of phloroglucinol with methyl sulphate and potassium hydroxide. This method, however, did not give satisfactory yields of the desired substance, a considerable part of the material being converted into a neutral oily product. The latter distilled at 140–145°/13 mm., or at 258–266° under the ordinary pressure. It was unchanged by further treatment with methyl sulphate and potassium hydroxide, but was not further investigated. The method employed by Will (*loc. cit.*) was therefore adopted, but with the employment of methyl sulphate instead of methyl iodide. In this way satisfactory yields of phloroglucinol trimethyl ether (m. p. 52°) were obtained.

Action of Acetyl Chloride and Aluminium Chloride on Phloroglucinol Trimethyl Ether.

Friedländer and Schnell (*loc. cit.*) treated phloroglucinol trimethyl ether with acetyl chloride and aluminium chloride, and obtained thereby 2-hydroxy-4:6-dimethoxyacetophenone and the corresponding trimethoxy-ketone. The present authors, however, when employing the method of these investigators, could isolate

from the reaction mixture only a small amount of 2-hydroxy-4:6-dimethoxyacetophenone, unchanged phloroglucinol trimethyl ether, and a *hydroxydiacetyldimethoxybenzene*, $C_{12}H_{14}O_6$, no matter how the conditions of the experiment were varied.

A quantity (11.5 grams) of phloroglucinol trimethyl ether was dissolved in carbon disulphide, 6 grams of acetyl chloride added, and then 10 grams of powdered aluminium chloride gradually introduced. After heating the mixture for one hour the solvent was decanted, and the residue decomposed with ice and hydrochloric acid. The product so obtained was dissolved in ether and shaken with a solution of potassium hydroxide, which removed the greater part of the material. The neutral product remaining in the ether consisted almost entirely of unchanged phloroglucinol trimethyl ether. The alkaline extracts were acidified, and the precipitated product was crystallised, first from ether, and then from alcohol, when it formed long, slender prisms, melting at $127-128^{\circ}$:

0.1090 gave 0.2407 CO_2 and 0.0583 H_2O . $C=60.2$; $H=5.9$.

0.1130 " 0.2491 CO_2 " 0.0595 H_2O . $C=60.1$; $H=5.9$.

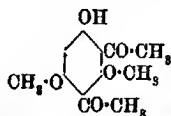
0.1316 " 0.2924 CO_2 " 0.0714 H_2O . $C=60.6$; $H=6.0$.

$OH \cdot C_6H_2(OMe)_2(CO \cdot CH_3)_2$ requires $C=61.2$; $H=6.1$ per cent.

$OH \cdot C_6H(OMe)_2(CO \cdot CH_3)_2$ " $C=60.5$; $H=5.9$ "

$OH \cdot C_6(OMe)_2(CO \cdot CH_3)_3$ " $C=60.0$; $H=5.7$ "

These analyses indicate that the substance under consideration was a *hydroxydiacetyldimethoxybenzene*, $OH \cdot C_6H(OMe)_2(CO \cdot CH_3)_2$, and this conclusion was subsequently confirmed by the analysis of its benzoyl derivative. No direct proof of the constitution of the diketone was obtained, but it would appear most probable that it is represented as follows:



This formula is preferred to the other possible one, as it is known that 2:4:6-trimethoxyacetophenone, which must first be formed, readily yields 2-hydroxy-4:6-dimethoxyacetophenone in the presence of aluminium chloride, and a second acetyl group, when entering the nucleus of the latter ketone, would assuredly enter the para-position with respect to the hydroxyl group.

Hydroxydiacetyldimethoxybenzene is sparingly soluble in ether, and moderately so in alcohol. It did not lose either of the methyl groups when treated with anhydrous ferric chloride or with aluminium chloride, and attempts to introduce a third acetyl group into the nucleus of it were unsuccessful.

Acetoxydiacetyldimethoxybenzene, $\text{OAc}\cdot\text{C}_6\text{H}(\text{OMe})_2(\text{CO}\cdot\text{CH}_3)_2$.—The *acetyl* derivative of the above-described compound was prepared by means of acetic anhydride. It crystallised from its concentrated solution in this solvent, and was purified by recrystallisation* from benzene. *Acetoxydiacetyldimethoxybenzene* forms well-defined prisms, melting at 150.5° :

0.1132 gave 0.2409 CO_2 and 0.0572 H_2O . $\text{C}=60.0$; $\text{H}=5.6$.

$\text{C}_{14}\text{H}_{16}\text{O}_6$ requires $\text{C}=60.0$; $\text{H}=5.7$ per cent.

This substance cannot be crystallised from ordinary alcohol or other hydrous solvents, as it is rapidly hydrolysed when dissolved in such liquids.

Benzoyloxydiacetyldimethoxybenzene, $\text{OBz}\cdot\text{C}_6\text{H}(\text{OMe})_2(\text{CO}\cdot\text{CH}_3)_2$.—This compound was prepared by the Schotten-Baumann reaction. It crystallised from benzene in cubes, and from absolute alcohol in slender prisms, melting at 179° :

0.1132 gave 0.2763 CO_2 and 0.0551 H_2O . $\text{C}=66.7$; $\text{H}=5.4$.

$\text{C}_{19}\text{H}_{22}\text{O}_6$ requires $\text{C}=66.7$; $\text{H}=5.3$ per cent.

The analysis of this compound conclusively confirms the results obtained by the analysis of the original hydroxy-diketone, inasmuch as the related compounds containing one and three acetyl groups would require $\text{C}=65.6$ and $\text{C}=63.0$ per cent. respectively.

Hydroxydiacetyldimethoxybenzenephnylhydrazone.—One gram of hydroxydiacetyldimethoxybenzene was dissolved in a small amount of alcohol, and slightly more than two molecular proportions of freshly distilled phenylhydrazine dissolved in acetic acid added. The mixture was heated on a water-bath for a quarter of an hour, when, after concentration, a crystalline product separated. This was collected, and crystallised many times, first from acetic acid, and subsequently from a mixture of ethyl acetate and alcohol, when the melting point gradually rose from 215° to 230° , the product finally obtained forming hexagonal prisms melting sharply at the latter temperature:

0.0927 gave 0.2248 CO_2 and 0.0529 H_2O . $\text{C}=66.1$; $\text{H}=6.3$.

0.1012 „ 8.4 c.c. N_2 (moist) at 19° and 753 mm. $\text{N}=9.4$.

$\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$ requires $\text{C}=65.8$; $\text{H}=6.1$; $\text{N}=8.5$ per cent.

This compound was therefore a *monophenylhydrazone* of hydroxydiacetyldimethoxybenzene.

The original ethereal mother liquors from the hydroxydiacetyldimethoxybenzene yielded a small amount of a substance which, when crystallised from alcohol, melted at 80° :

0.0754 gave 0.1685 CO_2 and 0.0425 H_2O . $\text{C}=61.2$; $\text{H}=6.3$.

$\text{C}_{10}\text{H}_{12}\text{O}_4$ requires $\text{C}=61.2$; $\text{H}=6.1$ per cent.

This substance was evidently 2-hydroxy-4:6-dimethoxyacetophenone, described by Friedländer and Schnell (*loc. cit.*).

Since no trimethoxyacetophenone could be obtained by means of the aluminium chloride reaction, recourse was had to the use of sublimed ferric chloride (Kostanecki, *Ber.*, 1899, **32**, 2261). By this means a good yield of product was obtained, which consisted largely of 2:4:6-trimethoxyacetophenone (m. p. 99–100°), but contained a little of the previously described hydroxydiacetyl-dimethoxybenzene.

Condensation of 2:4:6-Trimethoxyacetophenone with Vanillin Methyl Ether. Formation of 2:4:6-Trimethoxyphenyl 3:4-Dimethoxystyryl Ketone.

Vanillin was methylated by means of methyl sulphate in the manner described by Perkin and Weizmann (*Trans.*, 1906, **89**, 1649), when vanillin methyl ether was readily obtained. One molecular proportion of the latter compound was then heated in dry ethereal solution with equivalent amounts of 2:4:6-trimethoxyacetophenone and finely divided sodium.* Hydrogen was slowly evolved, and, after six hours, a yellow solid commenced to separate. When the reaction was complete, which was after about twenty-four hours heating, the ether was decanted, and the residue dissolved in benzene and washed with water. Considerable difficulty was originally experienced in causing the yellow, viscid residue obtained on evaporating the benzene to crystallise, but this was eventually effected from alcoholic solution, after which subsequent batches of material quickly crystallised on inoculating with the solid first obtained. 2:4:6-Trimethoxyphenyl 3:4-dimethoxystyryl ketone forms stout, pale yellow prisms, which contain one molecule of alcohol of crystallisation, and melt at 85°. The anhydrous substance melts at 117.5°:

0.1158 † gave 0.2778 CO₂ and 0.1158 H₂O. C = 65.4; H = 7.1.

0.1436 † „ 0.3512 CO₂ „ 0.0796 H₂O. C = 66.7; H = 6.1.

1.0010, † on heating at 100°, lost 0.1140 EtOH. EtOH = 11.4.

C₂₀H₂₂O₆, EtOH requires C = 65.3; H = 6.9; EtOH = 11.4 per cent.

C₂₀H₂₂O₆ requires C = 67.0; H = 6.1 per cent.

2:4:6-Trimethoxyphenyl 3:4-dimethoxystyryl ketone is very readily soluble in benzene, xylene, chloroform, or acetic acid, moderately so in alcohol or carbon disulphide, and almost insoluble in ether or petroleum. It also dissolves readily in moderately concentrated hydrochloric or sulphuric acids, yielding deep red

* Prepared by violently shaking molten sodium under xylene, the latter being subsequently removed by the addition of pure ether, and decantation.

† Air-dried.

‡ Anhydrous substance.

solutions. It distils without decomposition at $325^{\circ}/13$ mm., solidifying to a yellow, vitreous mass.

A quantity of the ketone was heated for five hours with a large excess of a concentrated alcoholic solution of potassium hydroxide. The greater part of the material was recovered unchanged after this treatment, but some veratric acid was isolated from the reaction mixture. It thus appears that, under the influence of potassium hydroxide, the ketone in question is attacked at the double linking, just as has been shown, in the preceding paper, to be the case with monomethylhomoeriodictyol. The first product of this change is, doubtless, vanillin methyl ether, which yields the veratric acid by the further action of the alkali.

*Action of Aluminium Chloride on 2: 4: 6-Trimethoxyphenyl
3: 4-Dimethoxystyryl Ketone.*

With the endeavour to remove methyl groups from the above-described ketone, in order to see if, in this way, homoeriodictyol could be obtained, the effect of ferric and aluminium chlorides on the pentamethoxy-compound was investigated. Ferric chloride was quite without action on it, but when heated with aluminium chloride it slowly lost one methyl group. The change was by no means complete, even after many hours' heating, but the hydrolysed product was readily separated from the unchanged material by boiling the mixture with successive portions of dilute aqueous potassium hydroxide. The alkaline liquids so obtained yielded, on acidification, a yellow compound, which crystallised very readily from alcohol in deep golden-coloured plates, melting at 154° :

0.1122 gave 0.2724 CO_2 and 0.0584 H_2O . $\text{C} = 66.2$; $\text{H} = 5.8$.

$\text{C}_{13}\text{H}_{20}\text{O}_6$ requires $\text{C} = 66.3$; $\text{H} = 5.8$ per cent.

This compound is doubtless identical with the 2-hydroxy-4: 6-dimethoxyphenyl 3: 4-dimethoxystyryl ketone (m. p. 157°) prepared in another way by Kostanecki (*Ber.*, 1904, **37**, 793), but the present authors were unable to obtain the crystalline acetyl derivative described by him, although several attempts were made.

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CCXVIII.—*The Molecular Complexity, in the Liquid State, of Tervalent Nitrogen Compounds.*

By WILLIAM ERNEST STEPHEN TURNER and ERNEST WYNDHAM MERRY.

IN a review of the possible causes of association in the amides by Dr. A. N. Meldrum and one of us (Trans., 1908, 93, 876), it was suggested that the association observed might well be due to the presence of the tervalent nitrogen atom or the oxygen atom of the group $\cdot\text{CO}\cdot\text{NH}_2$, and the observations recorded in this communication were, in the main, carried out in order to test this suggestion.

Evidence bearing directly on the problem should be obtainable by an examination of the molecular complexity of the amines, for in these substances the nitrogen atom can pass with great readiness from the ter- to the quinque-valent state. Such data as existed at the beginning of the work were but meagre, consisting of determinations, either in solution or in the liquid state, of the molecular weight of aniline, two or three of its derivatives, and of the toluidines (Auwers and Pelzer, *Zeitsch. physikal. Chem.*, 1897, 23, 449; Auwers and Dohrn, *ibid.*, 1899, 30, 542; Dutoit and Friderich, *Compt. rend.*, 1900, 130, 327). It is well known, however, and our research confirms the fact, that the molecular association of an aromatic substance is either considerably less than in the corresponding aliphatic compound, or is non-existent. We decided accordingly, whilst including a number of aromatic substances, to make a study of the aliphatic amines.

The research was extended, however, beyond a comparison of the amines and amides, and was made to include a survey of other nitrogen-containing compounds. Of these, some, notably aceto-, propio-, butyro-, and benzo-nitrile, had already been examined by several investigators (Ramsay and Shields, Trans., 1893, 63, 1089; Dutoit and Friderich, *loc. cit.*; Guye and Baud, *Arch. Sci. phys. nat.*, 1901, [iv], 11, 449; Renard and Guye, *J. Chim. phys.*, 1907, 5, 97), although their results do not in all cases agree as well as might be expected. We have included in our work redeterminations with these four substances, but have not given full results in each case.

As regards the nitro-compounds, Ramsay and Shields (*loc. cit.*) have proved, by a comparison of nitroethane and nitrobenzene, that aliphatic nitro-compounds are associated, whilst aromatic compounds are non-associated. The observations on this class of substances we have not extended, but the possibility of association connected with

the nitroso-group, as revealed by the tendency of a few derivatives of hydrocarbons to form double molecules at low temperatures (Piloty, *Ber.*, 1898, **31**, 452; Bamherger and Rising, *Ber.*, 1901, **34**, 3877), attracted us to examine three nitrosoamines, of which dimethylnitrosoamine is of particular interest on account of its considerable conductivity, solvent power, and dielectric constant (Walden, *Zeitsch. physikal. Chem.*, 1903, **46**, 103). From the high value of the dielectric constant we expected to find association.

The determination of the molecular complexities in the liquid state, rather than in solution, was attended by certain advantages, for our results render it possible to make a comparison, in some cases, with the extent of association in solution; and we have also been able to include a number of substances the solubilities of which in benzene and similar solvents are very slight, the advantage of being able to include formamide being considerable. As far as possible, the experiments have been carried out over the same range of temperatures.

Against these advantages, we have to set off the fact that the calculation and interpretation of the results by the Ramsay and Shields' method, which has been used in its original form, is open to objection, and our own determinations support those of Dutoit and Friderich and of Guye and his pupils in demonstrating that the Ramsay and Shields' formula can only be applied within somewhat circumscribed limits. We have not been able, owing to lack of data in most cases, to employ any of the alternative methods of determining the molecular complexity, such as have been suggested by Ramsay (*Proc. Roy. Soc.*, 1894, **56**, 175) and Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 184).

EXPERIMENTAL

The measurement of surface tension was carried out in an apparatus of the U-tube type, the capillaries used in the construction being previously carefully tested and calibrated at different points. In form, the apparatus was very similar to that employed by Hewitt and Winmill (*Trans.*, 1907, **91**, 441)—reference to their diagram will serve to explain our arrangement—but differed from it in two respects: the capillary tube was backed by enamel, and, more important still, the end of the capillary tube, to the extent of about one inch, was bent sharply downwards, and a piece of quill tubing of the same diameter fused on to it, this added tube being bent sharply upwards so as to be parallel both with the capillary and with the wide limb of the U-tube. The object of this elbow of quill tubing was twofold. It served, in the first place, as a trap

for particles falling from the rubber connexions, and, in the second place, as a reservoir into which liquid could be transferred from the capillary.

Constant temperatures were obtained by the use of large baths and a carefully regulated flame. At the higher temperatures we employed a bath of paraffin wax (m. p. 60°), finding it much preferable to concentrated sulphuric acid, and we were able to use it at temperatures up to 210° .

In most of the experiments, the air was removed from the apparatus by exhaustion to a low pressure, although it has been shown by Renaud and Guye (*loc. cit.*) that unless the substance is easily oxidisable, measurements of the surface tension made both in presence and in absence of air agree to within about $\frac{1}{2}$ per cent.

At each temperature, three readings of the capillary rise were made by means of a reading micrometer, the differences never amounting to more than four hundredths of a millimetre. A fresh surface was obtained for each reading by tilting the tube and allowing liquid to run from the capillary into the elbow of quill tubing. The substances of high melting point could not be treated in this way, and in these cases a fresh surface was obtained by temporarily forcing the liquid from the capillary into the wide tube. Two independent series of determinations of the surface tension were made with each substance, in many cases by employing two tubes and placing them side by side in the same bath.

The density determinations were mainly made in specific gravity bottles of 10 c.c. capacity, calibrated at five or six different temperatures between 20° and 90° , so that the volumes at other temperatures could be deduced. At the higher temperatures considerable difficulty was experienced in using this form of pyknometer, and the simple form shown in the diagram was devised and employed, the narrow tubing being capillary of 1–1.5 mm. diameter of quill tubing of about the same bore. The cup was charged with the solid, and the pyknometer transferred to the heating bath. The liquid level was adjusted by air pressure to the mark *b*, excess above the level *a* removed by fine capillary tubes, and the cup wiped out before weighing. All densities are compared with that of water at 4° .

With the exception of benzamide and salicylamide, the materials were obtained by purchase, mainly from Kahlbaum, and all were



subjected to purification save a pure specimen of phenylhydrazine obtained from Kahlbaum.

The liquid amines were treated with solid sodium or potassium hydroxide, and afterwards distilled, benzyl, dibenzyl, and triamylamine under diminished pressure, the others under atmospheric pressure. Distillates of constant, or almost constant, boiling point were obtained and used throughout. Diphenylamine and tribenzylamine were crystallised from alcohol until of constant melting point. Wherever possible, the densities obtained were compared with those of other investigators. The density of the aniline employed agreed exactly with that found by Brühl (*Zeitsch. physikal. Chem.*, 1895, 16, 193); and those of propyl-, dipropyl-, and tripropylamine were in very close agreement with the numbers given by Perkin (*Trans.*, 1889, 55, 693).

The nitrosoamines (from Schuchardt) were treated as follows: phenylmethylnitrosoamine with freshly heated sodium sulphate, the two others with recently ignited potassium carbonate, and subsequently distilled under diminished pressure.

Of the nitriles, acetonitrile, benzonitrile, phenylacetonitrile, and *m*-toluonitrile were treated with phosphoric oxide and afterwards distilled, the acetonitrile under atmospheric, the others under diminished pressure. Propio-, butyro-, and isobutylacetonitrile were kept over sodium sulphate, and then distilled under atmospheric pressure. Lacto-, mandelo- and *o*-toluonitrile were merely distilled under diminished pressure. The melting point of the *p*-toluonitrile was 28.4°, and the substance was used without further purification. The densities at 20° of acetonitrile and benzonitrile agreed very closely with the values found by Brühl (*loc. cit.*), but those of propio- and isobutylacetonitrile were a little higher, that of phenylacetonitrile a little lower, than Brühl found.

The formamide was well dried over sodium sulphate and afterwards distilled under diminished pressure. Its density at 20° was in good agreement with that given by Brühl. The other amides, the anilides and urethanes were purified by methods already described (Meldrum and Turner, this vol., p. 1007). At the conclusion of the surface-tension measurements, the melting points of the salicylamide and phenylacetamide were tested, and found to agree exactly with those of the original substances.

In addition to the amides on which we have been successful in making measurements, we endeavoured to bring into the scope of the work a number of diamides and ethyl oxamate, but found them all unstable. Carbamide decomposed at its melting point; ammonia from malonamide could be detected even before melting; whilst ethyl oxamate, when gradually heated, gave ammonia at 130°.

Neither could we find a suitable solvent for these substances. Their insolubility in benzene, ether, etc., is well known. Lachman (*Zeitsch. physikal. Chem.*, 1897, 22, 170) found that ethyl oxamate is soluble in methyl oxalate, and, in this solvent, gave molecular-weight values indicative of decided association. We used methyl oxalate, ethyl oxalate, diphenylamine, and phenylurethane in attempts to dissolve carhamide, oxamide, malonamide, and succinamide, but found all these amides either insoluble or only slightly soluble. We possess indirect evidence, however, showing that these substances should be classed as associated.

In the following tables are recorded the molecular weight of the substance, the temperature (t), the capillary rise in cm. (h), the radius of the tube in mm. (r), the density (ρ), the surface tension (γ), the values k_1 and k_2 of the Ramsay and Shields' constants calculated from the separate experiments, k , the mean values, and the degree of association (x).

In the case of formamide the mean values of k are derived from four sets of experiments.

Amines.

n-Propylamine (M. W. = 59).

| t . | h . | r . | ρ . | γ . | k_1 . | k_2 . | k . | x . |
|-------|-------|--------|----------|------------|---------|---------|-------|-------|
| 10° | 3.646 | 0.1779 | 0.7271 | 23.13 | — | — | — | — |
| 20° | 3.596 | 0.1779 | 0.7185 | 21.98 | 1.83 | 1.85 | 1.84 | 1.24 |
| 30° | 3.568 | 0.1779 | 0.7081 | 20.81 | 1.83 | 1.84 | 1.835 | 1.24 |
| 45° | 3.164 | 0.1780 | 0.6894 | 19.04 | 1.82 | 1.86 | 1.84 | 1.24 |

Dipropylamine (M. W. = 101).

| t . | h . | r . | ρ . | γ . | k_1 . | k_2 . | k . | x . |
|-------|-------|--------|----------|------------|---------|---------|-------|-------|
| 20° | 3.462 | 0.1779 | 0.7390 | 22.32 | — | — | — | — |
| 30° | 3.334 | 0.1799 | 0.7299 | 21.23 | 2.42 | 2.14 | 2.28 | 0.90 |
| 45° | 3.152 | 0.1780 | 0.7164 | 19.72 | 2.27 | 2.31 | 2.29 | 0.89 |
| 60° | 2.662 | 0.1780 | 0.7025 | 18.17 | 2.37 | 2.33 | 2.35 | 0.86 |

Tripropylamine (M. W. = 143).

| t . | h . | r . | ρ . | γ . | k_1 . | k_2 . | k . | x . |
|-------|-------|--------|----------|------------|---------|---------|-------|-------|
| 20° | 3.342 | 0.1850 | 0.7571 | 22.96 | — | — | — | — |
| 30° | 3.238 | 0.1851 | 0.7493 | 22.03 | 2.56 | 2.43 | 2.495 | 0.78 |
| 45° | 3.079 | 0.1851 | 0.7373 | 20.61 | 2.64 | 2.63 | 2.635 | 0.72 |
| 60° | 2.619 | 0.1851 | 0.7252 | 19.22 | 2.63 | 2.65 | 2.64 | 0.72 |
| 75° | 2.760 | 0.1851 | 0.7130 | 17.87 | 2.61 | 2.65 | 2.63 | 0.72 |

*iso*Amylamine (M. W. = 87).

| t . | h . | r . | ρ . | γ . | k_1 . | k_2 . | k . | x . |
|-------|-------|--------|----------|------------|---------|---------|-------|-------|
| 20° | 3.162 | 0.1851 | 0.7505 | 23.59 | — | — | — | — |
| 30° | 3.352 | 0.1851 | 0.7417 | 22.57 | 1.99 | 1.92 | 1.955 | 1.13 |
| 45° | 3.184 | 0.1851 | 0.7277 | 21.04 | 2.03 | 2.03 | 2.03 | 1.07 |
| 60° | 3.018 | 0.1851 | 0.7128 | 19.53 | 2.00 | 2.03 | 2.015 | 1.08 |

Triamylamine (M. W. = 227).

| t . | h . | r . | ρ . | γ . | k_1 . | k_2 . | k . | x . |
|-------|-------|--------|----------|------------|---------|---------|-------|-------|
| 20° | 3.399 | 0.1851 | 0.7859 | 24.25 | — | — | — | — |
| 30° | 3.310 | 0.1851 | 0.7790 | 23.41 | 3.09 | 3.12 | 3.105 | 0.56 |
| 45° | 3.172 | 0.1851 | 0.7676 | 22.11 | 3.18 | 3.11 | 3.145 | 0.55 |
| 60° | 3.034 | 0.1851 | 0.7568 | 20.85 | 3.14 | 3.07 | 3.115 | 0.56 |
| 75° | 2.892 | 0.1851 | 0.7461 | 19.59 | 3.20 | 3.17 | 3.185 | 0.54 |

*Amines (continued).**Diphenylamine* (M.W. = 169).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 60° | 4.268 | 0.1777 | 1.0547 | 39.23 | — | — | — | — |
| 75 | 4.150 | 0.1778 | 1.0435 | 37.77 | 2.37 | 2.66 | 2.515 | 0.77 |
| 90 | 4.023 | 0.1778 | 1.0326 | 36.23 | 2.55 | 2.46 | 2.505 | 0.78 |
| 105 | 3.890 | 0.1778 | 1.0217 | 34.66 | 2.63 | 2.55 | 2.59 | 0.74 |

Benzylamine (M.W. = 107).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.358 | 0.1850 | 0.9813 | 39.07 | — | — | — | — |
| 30 | 4.298 | 0.1850 | 0.9727 | 37.94 | 2.09 | 2.07 | 2.08 | 1.03 |
| 45 | 4.155 | 0.1850 | 0.9597 | 36.17 | 2.19 | 2.05 | 2.12 | 1.00 |
| 60 | 4.015 | 0.1850 | 0.9463 | 34.49 | 2.12 | 2.05 | 2.085 | 1.03 |
| 75 | 3.872 | 0.1850 | 0.9333 | 32.81 | 2.28 | 2.17 | 2.225 | 0.97 |

Dibenzylamine (M.W. = 197).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.362 | 0.1850 | 1.0276 | 40.63 | — | — | — | — |
| 30 | 4.280 | 0.1850 | 1.0199 | 39.61 | 2.90 | 2.71 | 2.805 | 0.86 |
| 45 | 4.150 | 0.1850 | 1.0083 | 38.01 | 2.92 | 2.73 | 2.85 | 0.64 |
| 60 | 4.026 | 0.1850 | 0.9963 | 36.10 | 2.93 | 2.82 | 2.875 | 0.63 |
| 75 | 3.894 | 0.1850 | 0.9844 | 34.79 | 3.01 | 2.90 | 3.00 | 0.58 |

Tritylamine (M.W. = 287).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 95° | 3.707 | 0.1850 | 0.9912 | 33.34 | — | — | — | — |
| 105 | 3.623 | 0.1850 | 0.9850 | 32.43 | 3.42 | 3.40 | 3.41 | 0.49 |
| 120 | 3.501 | 0.1850 | 0.9741 | 30.97 | 3.59 | 3.46 | 3.525 | 0.47 |
| 135 | 3.378 | 0.1851 | 0.9632 | 29.54 | 3.57 | 3.59 | 3.58 | 0.46 |

Phenylhydrazine (M.W. = 108).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.572 | 0.1830 | 1.0378 | 45.55 | — | — | — | — |
| 30 | 4.480 | 0.1850 | 1.0299 | 44.31 | 2.18 | 2.16 | 2.17 | 0.97 |
| 45 | 4.322 | 0.1850 | 1.0177 | 42.27 | 2.47 | 2.27 | 2.37 | 0.85 |
| 60 | 4.179 | 0.1850 | 1.0053 | 40.10 | 2.23 | 2.16 | 2.195 | 0.95 |

Acetylhydrazine (M.W. = 74).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.259 | 0.1850 | 1.0069 | 38.97 | — | — | — | — |
| 30 | 4.173 | 0.1850 | 0.9965 | 37.73 | 1.74 | 1.75 | 1.745 | 1.34 |
| 45 | 4.029 | 0.1850 | 0.9813 | 35.89 | 1.85 | 1.86 | 1.855 | 1.22 |
| 60 | 3.858 | 0.1850 | 0.9654 | 33.80 | 1.94 | 1.93 | 1.935 | 1.15 |
| 75 | 3.692 | 0.1850 | 0.9491 | 31.80 | 1.97 | 1.92 | 1.945 | 1.14 |

Diethylacetosuccine (M.W. = 102).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 3.833 | 0.1850 | 0.9422 | 32.81 | — | — | — | — |
| 30 | 3.758 | 0.1850 | 0.9331 | 31.82 | 1.79 | 1.77 | 1.78 | 1.30 |
| 45 | 3.628 | 0.1850 | 0.9197 | 30.28 | 1.90 | 1.89 | 1.895 | 1.15 |
| 60 | 3.499 | 0.1851 | 0.9061 | 28.71 | 1.97 | 2.00 | 1.985 | 1.10 |
| 75 | 3.350 | 0.1851 | 0.8919 | 27.13 | 2.01 | 2.02 | 2.015 | 1.08 |

Phenylmethylnitrosamine (M.W. = 136).

| ℓ° | h | r | ρ | γ | k_1 | k_2 | k | z |
|--------------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.394 | 0.1850 | 1.1275 | 44.96 | — | — | — | — |
| 30 | 4.319 | 0.1850 | 1.1187 | 43.75 | 2.38 | 2.30 | 2.34 | 0.86 |
| 45 | 4.182 | 0.1850 | 1.1055 | 41.95 | 2.40 | 2.43 | 2.415 | 0.82 |
| 60 | 4.048 | 0.1850 | 1.0919 | 40.11 | 2.49 | 2.51 | 2.50 | 0.73 |
| 75 | 3.916 | 0.1850 | 1.0782 | 38.31 | 2.45 | 2.48 | 2.465 | 0.80 |
| 90 | 3.782 | 0.1850 | 1.0644 | 36.53 | 2.47 | 2.55 | 2.51 | 0.78 |

*Nitriles.**Lactonitrile* (M.W. = 71).

| t° | h | r | ρ | γ | k_1 | k_2 | k | z |
|-----------|-------|--------|--------|----------|-------|-------|-------|------|
| 20° | 4.059 | 0.1850 | 0.9877 | 36.38 | — | — | — | — |
| 30 | 3.989 | 0.1850 | 0.9788 | 35.43 | 1.27 | 1.24 | 1.255 | 2.21 |
| 45 | 3.879 | 0.1850 | 0.9656 | 33.99 | 1.31 | 1.33 | 1.32 | 2.04 |
| 60 | 3.765 | 0.1850 | 0.9525 | 32.54 | 1.35 | 1.30 | 1.325 | 2.08 |

Butyronitrile (M.W. = 69).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 3.692 | 0.1780 | 0.7936 | 26.97 | — | — | — | — |
| 30 | 3.780 | 0.1780 | 0.7842 | 25.88 | 1.73 | 1.70 | 1.715 | 1.38 |
| 45 | 3.608 | 0.1779 | 0.7701 | 24.25 | 1.77 | 1.79 | 1.78 | 1.30 |
| 60 | 3.431 | 0.1779 | 0.7556 | 22.62 | 1.78 | 1.77 | 1.775 | 1.31 |

isoButylacetonitrile (M.W. = 97).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 3.637 | 0.1850 | 0.8038 | 26.53 | — | — | — | — |
| 30 | 3.548 | 0.1850 | 0.7955 | 25.61 | 1.80 | 1.81 | 1.805 | 1.27 |
| 45 | 3.410 | 0.1851 | 0.7827 | 24.23 | 1.83 | 1.85 | 1.84 | 1.24 |
| 60 | 3.268 | 0.1851 | 0.7699 | 22.84 | 1.89 | 1.87 | 1.88 | 1.20 |

Benzonitrile (M.W. = 105).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 4.407 | 0.1778 | 1.0051 | 33.59 | — | — | — | — |
| 30 | 4.315 | 0.1777 | 0.9974 | 32.51 | 1.93 | 1.95 | 1.94 | 1.14 |
| 45 | 4.176 | 0.1777 | 0.9831 | 30.78 | 2.04 | 2.08 | 2.055 | 1.06 |
| 60 | 4.010 | 0.1778 | 0.9692 | 28.89 | 2.32 | 2.25 | 2.285 | 0.99 |

Phenylacetonitrile (M.W. = 117).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 4.488 | 0.1550 | 1.0157 | 41.36 | — | — | — | — |
| 30 | 4.404 | 0.1850 | 1.0076 | 40.27 | 2.69 | 2.67 | 2.68 | 1.03 |
| 45 | 4.276 | 0.1850 | 0.9939 | 38.56 | 2.14 | 2.13 | 2.135 | 0.99 |
| 60 | 4.136 | 0.1850 | 0.9792 | 36.75 | 2.32 | 2.29 | 2.315 | 0.88 |

Mandelonitrile (M.W. = 133).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 4.515 | 0.1776 | 1.1165 | 43.91 | — | — | — | — |
| 30 | 4.350 | 0.1776 | 1.1086 | 42.98 | 1.78 | 1.87 | 1.825 | 1.25 |
| 45 | 4.346 | 0.1776 | 1.0966 | 41.52 | 1.87 | 1.89 | 1.88 | 1.20 |
| 60 | 4.234 | 0.1777 | 1.0814 | 40.02 | 1.96 | 1.93 | 1.945 | 1.14 |

o-Toluenitrile (M.W. = 117).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 4.189 | 0.1850 | 0.9855 | 37.84 | — | — | — | — |
| 30 | 4.100 | 0.1850 | 0.9863 | 36.70 | 2.21 | 2.21 | 2.21 | 0.94 |
| 45 | 3.961 | 0.1850 | 0.9737 | 35.00 | 2.25 | 2.33 | 2.29 | 0.89 |
| 60 | 3.809 | 0.1850 | 0.9596 | 33.17 | 2.35 | 2.27 | 2.36 | 0.85 |
| 75 | 3.656 | 0.1850 | 0.9481 | 31.46 | 2.39 | 2.32 | 2.355 | 0.85 |

m-Toluenitrile (M.W. = 117).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|------|------|
| 20° | 4.689 | 0.1778 | 1.0316 | 36.79 | — | — | — | — |
| 30 | 4.612 | 0.1778 | 1.0235 | 35.81 | 1.84 | 1.84 | 1.84 | 1.21 |
| 45 | 3.890 | 0.1778 | 1.0122 | 34.34 | 1.91 | 1.91 | 1.91 | 1.17 |
| 60 | 3.769 | 0.1778 | 0.9997 | 32.78 | 2.03 | 1.99 | 2.01 | 1.08 |
| 75 | 3.624 | 0.1779 | 0.9872 | 31.22 | 2.07 | 2.05 | 2.06 | 1.04 |

p-Toluenitrile (M.W. = 117).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 30° | 4.112 | 0.1850 | 0.9785 | 36.51 | — | — | — | — |
| 45 | 3.978 | 0.1850 | 0.9640 | 34.80 | 2.22 | 2.21 | 2.215 | 0.94 |
| 60 | 3.846 | 0.1850 | 0.9512 | 33.20 | 2.13 | 2.22 | 2.175 | 0.86 |
| 75 | 3.701 | 0.1850 | 0.9390 | 31.64 | 2.29 | 2.17 | 2.23 | 0.98 |

*Amides.**Formamide* (M.W. = 45).

| t° | h | r | p | γ | k_1 | k_2 | k | z |
|-----------|-------|--------|--------|----------|-------|-------|------|------|
| 20° | 5.812 | 0.1772 | 1.1350 | 57.35 | — | — | — | — |
| 30 | 5.770 | 0.1772 | 1.1267 | 56.51 | 0.65 | 0.61 | 0.63 | 6.18 |
| 45 | 5.704 | 0.1773 | 1.1142 | 55.27 | 0.61 | 0.65 | 0.66 | 5.76 |
| 60 | 5.634 | 0.1773 | 1.1015 | 53.94 | 0.73 | 0.73 | 0.74 | 4.85 |
| 75 | 5.529 | 0.1773 | 1.0892 | 52.36 | 0.93 | 0.94 | 0.95 | 3.34 |

Acetamide (M.W. = 59).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 85° | 4.300 | 0.1850 | 0.9986 | 38.96 | — | — | — | — |
| 95 | 4.226 | 0.1850 | 0.9904 | 37.98 | 1.18 | 1.14 | 1.16 | 2.97 |
| 105 | 4.147 | 0.1850 | 0.9822 | 36.86 | 1.24 | 1.17 | 1.205 | 2.33 |
| 120 | 4.020 | 0.1850 | 0.9703 | 35.39 | 1.31 | 1.27 | 1.29 | 2.11 |

Propionamide (M.W. = 73).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 80° | 3.796 | 0.1778 | 0.9597 | 31.77 | — | — | — | — |
| 90 | 3.718 | 0.1779 | 0.9517 | 30.88 | 1.29 | 1.33 | 1.31 | 2.00 |
| 105 | 3.599 | 0.1779 | 0.9395 | 29.50 | 1.25 | 1.31 | 1.33 | 2.01 |
| 120 | 3.478 | 0.1779 | 0.9272 | 28.14 | 1.36 | 1.37 | 1.365 | 1.94 |

Butyramide (M.W. = 89).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 80° | 4.272 | 0.1850 | 1.1581 | 44.12 | — | — | — | — |
| 90 | 4.226 | 0.1850 | 1.1301 | 43.34 | 1.06 | 1.04 | 1.05 | 2.87 |
| 105 | 4.152 | 0.1850 | 1.1151 | 42.13 | 1.12 | 1.13 | 1.125 | 2.59 |
| 120 | 4.076 | 0.1850 | 1.1062 | 40.91 | 1.13 | 1.15 | 1.14 | 2.34 |

Isobutyramide (M.W. = 121).

| | | | | | | | | |
|------|-------|--------|--------|-------|------|------|-------|------|
| 130° | 3.886 | 0.1850 | 1.0792 | 35.06 | — | — | — | — |
| 140 | 3.816 | 0.1850 | 1.0717 | 37.10 | 1.11 | 1.08 | 1.065 | 2.70 |
| 150 | 3.804 | 0.1850 | 1.0641 | 39.73 | 1.16 | 1.26 | 1.21 | 2.02 |
| 160 | 3.758 | 0.1850 | 1.0565 | 36.01 | 1.29 | 1.25 | 1.27 | 2.16 |
| 170 | 3.702 | 0.1850 | 1.0489 | 35.23 | 1.43 | 1.43 | 1.43 | 1.61 |

Phenylacetamide (M.W. = 135).

| | | | | | | | | |
|------|-------|--------|--------|-------|------|------|-------|------|
| 160° | 3.644 | 0.1850 | 1.0179 | 33.66 | — | — | — | — |
| 170 | 3.587 | 0.1850 | 1.0105 | 32.89 | 1.58 | 1.51 | 1.545 | 1.61 |
| 180 | 3.522 | 0.1850 | 1.0029 | 32.05 | 1.77 | 1.70 | 1.735 | 1.63 |

Salicylamide (M.W. = 137).

| | | | | | | | | |
|------|-------|--------|--------|-------|------|------|------|------|
| 140° | 3.755 | 0.1850 | 1.1719 | 49.35 | — | — | — | — |
| 150 | 3.716 | 0.1850 | 1.1663 | 39.64 | 1.22 | 1.18 | 1.20 | 2.35 |
| 160 | 3.700 | 0.1850 | 1.1578 | 38.87 | 1.40 | 1.36 | 1.38 | 1.90 |
| 170 | 3.648 | 0.1850 | 1.1493 | 38.04 | 1.55 | 1.55 | 1.55 | 1.70 |

*Anilides and Urethanes.**Formanilide* (M.W. = 121).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 60° | 3.871 | 0.1850 | 1.1115 | 39.04 | — | — | — | — |
| 75 | 3.790 | 0.1850 | 1.0971 | 37.73 | 1.49 | 1.48 | 1.485 | 1.69 |
| 90 | 3.700 | 0.1850 | 1.0860 | 36.48 | 1.55 | 1.55 | 1.55 | 1.60 |
| 105 | 3.599 | 0.1850 | 1.0743 | 35.08 | 1.75 | 1.70 | 1.725 | 1.36 |

Acetanilide (M.W. = 135).

| | | | | | | | | |
|------|-------|--------|--------|-------|------|------|-------|------|
| 120° | 3.938 | 0.1778 | 1.0261 | 35.24 | — | — | — | — |
| 130 | 3.868 | 0.1778 | 1.0179 | 34.34 | 1.86 | 1.88 | 1.87 | 1.21 |
| 145 | 3.762 | 0.1778 | 1.0055 | 32.99 | 1.87 | 1.89 | 1.88 | 1.20 |
| 160 | 3.652 | 0.1779 | 0.9933 | 31.05 | 1.88 | 1.93 | 1.905 | 1.17 |

*Anilides and Urethanes (continued).**Methylacetanilide (M.W. = 149).*

| t° | h | r | ρ | γ | k_1 | k_2 | k | α |
|-------------|-------|--------|--------|----------|-------|-------|-------|----------|
| 105° | 3.524 | 0.1850 | 1.0036 | 32.09 | — | — | — | — |
| 115 | 3.448 | 0.1851 | 0.9951 | 31.15 | 2.14 | 2.22 | 2.18 | 0.96 |
| 120 | 3.406 | 0.1851 | 0.9910 | 30.65 | 2.22 | 2.21 | 2.215 | 0.94 |
| 130 | 3.330 | 0.1851 | 0.9828 | 29.71 | 2.24 | 2.24 | 2.24 | 0.92 |
| 145 | 3.206 | 0.1851 | 0.9703 | 28.24 | 2.33 | 2.27 | 2.30 | 0.88 |

The ranges of temperature for which the values of k are calculated are:—
105–115°; 105–120°; 115–130°; 130–145°.

Ethylacetanilide (M.W. = 163).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 60° | 3.600 | 0.1850 | 0.9988 | 34.27 | — | — | — | — |
| 75 | 3.681 | 0.1850 | 0.9798 | 32.73 | 2.46 | 2.46 | 2.46 | 0.80 |
| 90 | 3.554 | 0.1850 | 0.9657 | 31.15 | 2.58 | 2.49 | 2.535 | 0.76 |
| 105 | 3.424 | 0.1851 | 0.9516 | 29.58 | 2.59 | 2.60 | 2.595 | 0.74 |

Ethylurethane (M.W. = 89).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 20° | 3.311 | 0.1851 | 1.0459 | 31.47 | — | — | — | — |
| 75 | 3.205 | 0.1851 | 1.0313 | 30.01 | 1.51 | 1.48 | 1.495 | 1.69 |
| 90 | 3.095 | 0.1851 | 1.0162 | 28.56 | 1.53 | 1.51 | 1.52 | 1.65 |
| 105 | 2.989 | 0.1851 | 1.0005 | 27.07 | 1.58 | 1.56 | 1.57 | 1.57 |

Phenylurethane (M.W. = 165).

| | | | | | | | | |
|-----|-------|--------|--------|-------|------|------|-------|------|
| 60° | 3.680 | 0.1850 | 1.0792 | 36.04 | — | — | — | — |
| 75 | 3.576 | 0.1850 | 1.0677 | 34.65 | 2.18 | 2.15 | 2.165 | 0.97 |
| 90 | 3.468 | 0.1851 | 1.0538 | 33.18 | 2.25 | 2.19 | 2.22 | 0.93 |
| 105 | 3.354 | 0.1851 | 1.0399 | 31.67 | 2.39 | 2.41 | 2.40 | 0.83 |

The following results, which we do not consider it necessary to give in full, have also been obtained. *Acetonitrile*: 20–30°, $\alpha=1.47$, $r=1.73$; 30–45°, $k=1.53$, $\alpha=1.63$; 45–60°, $k=1.56$, $\alpha=1.58$, in good agreement with the values of Dutoit and Friderich (*loc. cit.*) and Renard and Guye (*loc. cit.*). *Propionitrile*: 20–30°, $\alpha=1.63$, $r=1.48$; 30–45°, $k=1.63$, $\alpha=1.48$; 45–60°, $k=1.66$, $\alpha=1.44$, agreeing substantially with the results of Ramsay and Shields and Renard and Guye, but not with those of Dutoit and Friderich. *Aniline*: 20–45°, $k=1.695$, $\alpha=1.40$; 45–75°, $\alpha=2.005$, $\alpha=1.09$, in agreement with Dutoit and Friderich.

We have also confirmed the abnormal result obtained by Dutoit and Friderich for diphenylamine:

In the case of ethylurethane, we have obtained values which agree well with those of Guye and Baud, but entirely different results with phenylurethane. The authors mentioned found, between 63.8° and 103.8°, $k=1.38$; and 103.8° and 152.8°, $k=1.81$, values indicative of pronounced association. In benzene solution, phenylurethane is but slightly associated, much less so than ethylurethane, which, at the lower range, Guye and Baud did not find associated as much as phenylurethane.

The general results are discussed in the sections below.

The Molecular Complexity of the Amines.

Broadly speaking, we may say that the primary amines are slightly associated, the secondary and tertiary amines non-associated in the liquid state. Such other data as exist confirm our conclusions. Thus, Kahlenberg (*J. Physical Chem.*, 1901, 5, 284), by measurement of Trouton's constant, found that amylamine is somewhat associated, but dipropylamine and diisobutylamine are normal. The measurements on aniline in naphthalene solution (Auwers and Pelzer, *loc. cit.*) and our own determinations in solution, quoted below, add further confirmation.

As is the case with other classes of associated substances, the extent of association diminishes with increase in the molecular weight. We deduce from this fact that the parent substance, ammonia, in the liquid state, should show pronounced association, and that the degree of association should be higher than found by Walden (*loc. cit.*, p. 196) (compare Franklin and Kraus, *Amer. Chem. J.*, 1899, 21, 8; *J. Physical Chem.*, 1907, 11, 558).

More exact interpretation of the results than is given in the preceding paragraph is somewhat difficult to make. If the primary amines are associated, are the secondary and tertiary amines, with their high values of k , dissociated?

Substances other than the amines are known having values of the Ramsay and Shields' constant higher than 2.12. Walden (*loc. cit.*, p. 212) quotes, from different sources, a number of such substances. Homfray and Guye (*J. Chim. phys.*, 1903, 1, 518) showed that in a series of esters examined the value of k increased with the complexity of the molecule, until, with pelargonyl malate, $k = 3.68$. The alteration in the value of k with constitution is perhaps more simply brought out with the amines than in the case of the esters. In the following summary, the values of k are given for the temperature range (except in the case of tribenzylamine) of 30—45°, and it is evident that in the amines the value increases with (1) the number of hydrogen atoms substituted, (2) the mass of the substituting group:

| | | | |
|-----------------------------|-------|----------------------|-----------------|
| <i>n</i> -Propylamine | 1.84 | Benzylamine | 2.12 |
| Dipropylamine | 2.29 | Dibenzylamine | 2.85 |
| Tripropylamine | 2.635 | Tribenzylamine | 3.58 (120—135°) |
| isoAmylamine | 2.03 | | |
| Triamylamine | 3.14 | | |

Reference to the anilides will show a similar regularity.

Homfray and Guye suggested that the high values of k obtained by them might be due either to the fact that the molecules were not spherical or to actual dissociation of the molecules, and they found support for the latter view from calculations based on

Longinescu's method (*J. Chim. phys.*, 1903, **1**, 296), and from the cryoscopic observations of Freundler (*Bull. Soc. chim.*, 1895, [iii], 13, 1055).

Other methods of testing the molecular complexity in the liquid state are, however, not in favour of the idea that dissociation occurs. Walden (*loc. cit.*), using a formula which he had found to be generally valid for non-associated liquids, showed that a number of the substances having high values of the Ramsay and Shields' constant did not differ from the well-recognised normal substances; whilst Kurbatoff and Eliséeff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1422) have pointed out that the esters examined by Homfray and Guye are normal according to the values of Trouton's constant which they possess.

Evidence of dissociation in the liquid state should be revealed, perhaps to a less extent, in solution, and the dissociation should increase with the concentration. We have, accordingly, determined the molecular weights, in benzene solution, of the amyl- and benzylamines. In the tables, the association factor, α , = $\frac{\text{M.W. (obs.)}}{\text{M.W. (calc.)}}$.

Molecular Weights in Benzene Solution.

(iso-Amylamine (M.W. = 87.1).

Solvent : 15.03 grams.

| w (grams). | Δ° . | M.W. (obs.). | α . |
|--------------|------------------|--------------|------------|
| 0.2916 | 1.091 | 88.9 | 1.022 |
| 0.6253 | 1.753 | 90.7 | 1.116 |
| 0.9092 | 3.205 | 103.1 | 1.185 |
| 1.375 | 4.895 | 104.1 | 1.196 |

Triamylamine (M.W. = 227.3).

Solvent : 14.83 grams.

| w (grams). | Δ° . | M.W. (obs.). | α . |
|--------------|------------------|--------------|------------|
| 0.2912 | 0.337 | 219.2 | 0.97 |
| 0.5592 | 0.833 | 226.3 | 1.00 |
| 1.035 | 1.495 | 230.3 | 1.03 |
| 1.293 | 1.858 | 234.7 | 1.034 |

Benzylamine (M.W. = 107.1).

Solvent : 16.06 grams.

| w (grams). | Δ° . | M.W. (obs.). | α . |
|--------------|------------------|--------------|------------|
| 0.5582 | 1.568 | 110.4 | 1.03 |
| 0.7489 | 2.055 | 113.5 | 1.06 |
| 1.318 | 3.485 | 122.4 | 1.14 |
| 1.497 | 3.792 | 122.9 | 1.15 |

Dibenzylamine (M.W. = 197.1).

Solvent : 14.88 grams.

| w (grams). | Δ° . | M.W. (obs.). | α . |
|--------------|------------------|--------------|------------|
| 0.1395 | 0.253 | 185.3 | 0.94 |
| 0.4925 | 0.871 | 192.7 | 0.98 |
| 1.187 | 2.021 | 197.3 | 1.00 |
| 1.490 | 2.536 | 197.4 | 1.00 |

Tribenzylamine (M.W. = 287.2).

Solvent : 15.23 grams.

| w (grams). | Δ° . | M.W. (obs.). | α . |
|--------------|------------------|--------------|------------|
| 0.3406 | 0.402 | 278.3 | 0.97 |
| 0.7660 | 0.926 | 271.3 | 0.95 |
| 1.173 | 1.406 | 273.8 | 0.95 |
| 1.534 | 1.861 | 270.7 | 0.94 |

Our results afford further evidence that the primary amines are associated, but there is no evidence of any dissociation of triamylamine or dibenzylamine. The results with tribenzylamine are low, but in no way commensurate with the apparent dissociation in the fused state.

As a final test, we plotted the values of molecular surface energy against the temperature for triamylamine, dibenzyl- and tribenzylamine, since Dutoit and Friderich (*loc. cit.*) found that the coefficient of the molecular surface energy of the normal liquids which they examined was independent of the temperature. The following values were used:

Triamylamine, 1060.7; 1029.8; 982.1; 935.0; 887.0.
 Dibenzylamine, 1353.0; 1324.0; 1280.2; 1257.7; 1190.5.
 Tribenzylamine, 1460.0; 1425.8; 1372.0; 1318.4.

The temperatures are given in the tables (pp. 2073, 2074). In each case, the straight line joining the end-points passed, almost perfectly, through all the points.

We must conclude therefore that the abnormal results under discussion are due to the non-validity of the Ramsay and Shields' formula.

The Nitrosoamines and the Nitriles.

As in the nitro-compounds, so also in the nitroso-compounds here examined, association occurs only in the aliphatic series. The cause of association is to be connected with the nitroso-group, since the secondary and tertiary amines are non-associated.

The tendency of the nitriles to associate is also only marked in the aliphatic series. Benzonitrile has a slight tendency to association, and the property is exhibited distinctly by *m*-toluonitrile. The other aromatic nitriles, save mandelonitrile, which is associated, exhibit abnormally high values of *k*.

It will not escape notice that the introduction of a hydroxyl group into the substance considerably raises the association, as in lactonitrile and mandelonitrile (see also lactamide).

The Amides.

The amides in the liquid state are very strongly associated, and, unlike the nitriles, nitro- and nitroso-compounds, this association extends to the aromatic as well as to the aliphatic compounds. Indeed, the extent of association in benzamide and salicylamide is striking.

From the following table of association factors, it will be seen that the extent of association is roughly of the same order as that existing in the hydroxyl-containing substances—the organic acids and the alcohols. The data for the acids, alcohols, water, and phenol are taken from the papers of Ramsay and Shields (*loc. cit.*) and Ramsay and Aston (*Trans.*, 1894, 65, 168). Since data at

exactly comparable temperatures are not available, the actual temperatures are quoted:

| | | | |
|--|--|---|------|
| H ₂ O (20—30°) | 3.81 | | |
| CH ₃ ·OH (16—46°) | 8.43 | H·CO ₂ H (16—46°) | 3.61 |
| C ₂ H ₅ ·OH (16—46°) | 2.74 | CH ₃ ·CO ₂ H (16—46°) | 3.62 |
| C ₃ H ₇ ·OH (16—46°) | 2.25 | C ₂ H ₅ ·CO ₂ H (16—46°) | 1.77 |
| C ₆ H ₅ ·OH (46—78°) | 1.43 | | |
| | H·CO·NH ₂ (20—30°) | 6.18 | |
| | CH ₃ ·CO·NH ₂ (85—95°) | 2.47 | |
| | C ₂ H ₅ ·CO·NH ₂ (80—90°) | 2.06 | |
| | C ₆ H ₅ ·CO·NH ₂ (130—140°) | 2.70 | |

The outstanding feature of the results recorded is undoubtedly the high associative power exhibited by formamide. Walden (*Zeitsch. physikal. Chem.*, 1906, **54**, 180) expressed the belief that this substance is strongly associated, but made no measurement of its complexity save in aqueous solution, in which it possessed the normal molecular weight. Again (*Proc. Faraday Soc.*, 1910, 156), he states that "formamide appears to reproduce nearly all the valuable qualities of water." Save certain fused salts and sulphuric acid, formamide is more strongly associated than any other liquid yet examined. Its molecular complexity, however, decreases rapidly with rise of temperature. Between 20° and 75°, its complexity drops from 6.18 to 3.34, whilst that of water falls only from 3.44 to 2.9.

We suggested (*Proc.*, 1910, **26**, 128) that the solvent power of formamide for salts is connected with its high molecular complexity. Acetamide has also been found a solvent for salts (Walker and Johnson, *Trans.*, 1905, **88**, 1597; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1903, **40**, 1415). Formamide and acetamide can also, like water, produce hydrolysis of antimony trichloride (Bruni and Manuelli, *Zeitsch. Elektrochem.*, 1905, **11**, 554).

Passing to the anilides and urethanes, we note that association is diminished by substitution of hydrogen in the amido-group. The result with acetanilide was unexpected. The measurements of Auwers, of Beckmann, and of Meldrum and Turner, made on solutions of the anilides, show clearly that acetanilide is distinctly more associated than formanilide. Quite a different result is obtained on comparing the two substances in the liquid state.

The question whether the tervalent nitrogen atom is responsible for the association in the amides can, we believe, be regarded as answered in the negative. Methyl- and ethyl-acetanilide are non-associated, as also are secondary and tertiary amines, in all of which a tervalent nitrogen atom is still present. It is also obvious, from the results with methyl- and ethyl-acetanilide, that the oxygen atom does not bring about association (compare Meldrum and Turner, 1910, **97**, 1616), a conclusion in agreement with what is already known concerning esters, acid anhydrides, and ether.

Whatever the properties of chemical combination possessed by the nitrogen or oxygen atom, it appears clear that they cannot be held to be the cause of molecular association, and, in most cases, perhaps in all, association only occurs when these elements are present in distinct electronegative groups.

In the case of the amides, it appears that association is only possible when hydrogen is still present in the amide group. The power of molecular association disappears only when the hydrogen is eliminated from this group. Formamide and acetamide, also, like the hydroxylic substances methyl and ethyl alcohols, ethylene glycol, and glycerol, can combine with salts in the same way as water enters into union as water of crystallisation (Titherley, *Trans.*, 1901, **79**, 413; Walker and Johnson, *loc. cit.*; Menshutkin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010; Grün and Bockisch, *Ber.*, 1908, **41**, 3465; Röhler, *Zeitsch. Elektrochem.*, 1910, **16**, 419).

Such facts as these might be used as evidence in favour of the hydroxylic constitution of the amides. But the arguments against this theory are very weighty (Meldrum and Turner, *Trans.*, 1908, **93**, 890), and we have to remember that not only do water and formamide possess like properties, but liquid ammonia, an associated liquid, closely resembles water, can produce hydrolysis (ammonolysis, Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820), and, like water, can combine with salts.

It is difficult to locate the exact cause of the association in the amides. The apparent connexion between association and power of producing hydrolysis indicates another method by which the cause of association in the amides might conceivably be tested. If, in water, for example, the hydroxyl group is responsible both for the association produced and also for the hydrolysing power of water, then we might assume that the group in the amides which produces hydrolysis is also the cause of association. Bruni and Manuelli (*loc. cit.*) have found that when antimony trichloride is hydrolysed by formamide or acetamide, the entering group, which is equivalent to one chlorine atom, and therefore to the hydroxyl group, is $R \cdot CO \cdot NH$. Evidence of the nature of the action, if any, of the anilides and urethanes is desirable in this connexion.

Finally, our results bear out the general connexion between the degree of association and the dielectric constant of a liquid. Quite recently, Walden (*Zeitsch. physikal. Chem.*, 1910, **70**, 569) has pointed out that all substances with high dielectric constants possess certain electronegative groups, as OH, NO_2 , CO, CN, NH_2 , etc. Such groups we know to be present in those carbon compounds which exhibit association, and we should expect to find the dielectric constant and the degree of association run parallel. In the papers

already referred to, Walden has made comparison of the two properties. We quote the following values of the dielectric constant, in connexion with the fresh data brought forward in this communication: Formamide (20°), >84; acetamide (83°), 59.2; dimethylnitrosoamine (20°), 53.3; lactonitrile (20°), 37.7; formanilide (liquid), 20.5; acetanilide (liquid), 19.5; phenylacetoneitrile (21.5°), 18.2.

These numbers, and the more extensive comparisons by Walden, show that it is generally true that associated substances have high dielectric constants. The converse is by no means true, although, as may be seen, the substances of highest dielectric constant are those which have the highest association factors.

As regards dimethylnitrosoamine, it is quite possible, bearing in mind the abnormal results obtained with secondary and tertiary amines, that its degree of association is greater than our measurements reveal.

The connexion between the dielectric constant and the degree of association, although at best approximate, leads us, when taken in conjunction with the fact that the elements nitrogen and oxygen with unsaturated valencies do not appear of themselves to cause molecular association, to the conclusion that association in liquids is due to electrical rather than, as supposed by Guye and Baud (*Compt. rend.*, 1901, 132, 1555), to chemical forces.

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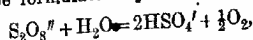
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CCXIX.—*The Dynamics of the Decomposition of Persulphuric Acid and its Salts in Aqueous Solution.*

By LEILA GREEN and ORME MASSON.

LEVI AND MIGLIORINI (*Gazzetta*, 1906, 36, ii, 599) have shown that potassium and sodium persulphates decompose in aqueous solution unimolecularly, and that the action is much accelerated by the addition of acids. Our own experiments confirm both of these results. It is, however, somewhat difficult to reconcile them with one another, for the action itself produces acid sulphate, and can, indeed, be followed throughout its course by the increasing

acidity, so that the curve should exhibit the features of an auto-accelerated, rather than those of an unmodified, unimolecular action. The difficulty, however, disappears if the acid sulphate product be assumed to ionise only into metal and HSO_4' , and to provide practically no H^+ ions, or if, in other words, sulphuric acid be regarded as a monobasic acid under the conditions of the experiments. The action may then be formulated by the equation:



which makes it strictly unimolecular in form. On general grounds the assumption may be objected to, but it does not appear possible to explain without it the behaviour of persulphuric acid and its salts, and it will be shown that one can, by its aid, co-ordinate the various results obtained with the acid, its potassium and sodium salts, its barium salt, and mixtures of these with each other, with other salts, and with acids. One or two unexplained difficulties remain, which will be dealt with in the sequel.

The persulphate solutions employed by us were obtained from solutions of the barium salt, prepared from commercial ammonium persulphate by treatment with excess of barium hydroxide in a vacuum and subsequent neutralisation with dilute sulphuric acid.

The initial strength of each persulphate solution was determined by measuring the final acidity produced by boiling a measured volume, the titrations being carried out with standard sodium hydroxide, using methyl-orange as indicator. Comparative tests were made in some cases by the ferrous sulphate and permanganate method, and also by gravimetric determinations of the metal as sulphate. The results in all cases agreed fairly well, but the acidimetric method was found to be the most accurate, besides having the advantage of rapidity. The progress of the decomposition in each experiment was also followed by acidimetry. In all cases the temperature of the thermostat was 80.0° , which was found to give a convenient rate of action, except in the experiments conducted at 70° and 90° for the purpose of fixing a temperature-coefficient. The solution was always divided at the outset into a number of 5 c.c. samples, and these were heated in closed tubes, according to the method described in a previous research on cyanates (Masson and Masson, *Zeitsch. physikal. Chem.*, 1910, 70, 290).

The persulphates which we have examined may be divided, for the present purpose, into three classes. The first contains those of sodium, potassium, and ammonium, which are neutral salts convertible into soluble acid sulphates. The magnesium salt properly belongs to this class, but differs somewhat in its behaviour from the other members. The second class contains persulphuric acid itself, which doubles its acidity by conversion into sulphuric acid.

The third class contains barium persulphate, which, originally neutral, produces persulphuric acid and insoluble barium sulphate. The course of the action is quite different in each of these classes, and they therefore require separate consideration.

In the sequel we have thought it desirable to economise space by suppressing most of the numerical details of our work, and have therefore given only the essential results, except where fuller treatment appeared necessary.

Class I.—Neutral Persulphates which form Soluble Acid Sulphates.

These cases conform to the equation for simple unimolecular action:

$$\frac{dx}{dt} = k_1(A - x), \text{ or } k_1 = \frac{1}{t_2 - t_1} \log_e \frac{A - x_1}{A - x_2},$$

where A is the initial concentration of persulphate, and $A - x$ is its value at any subsequent time, t . To avoid some slight uncertainty due to the time required to raise the tubes to the bath temperature, the time at which the first sample was taken from the bath was selected, rather than the moment of immersion, as t_1 . The values of k_1 given in table I are averages calculated in each case from several points in a curve covering nearly the whole course of the action. Separate values in any one experiment were found to agree well. It is evident that k_1 is but slightly dependent on the initial concentration, or even on the nature of the metallic radicle.

In this and subsequent tables, the concentrations are expressed in gram-molecules of persulphate per litre, and the times are measured in minutes:

TABLE I.

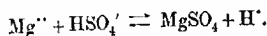
| Salt. | A . | k_1 . |
|---|-------|---------|
| $\text{Na}_2\text{S}_2\text{O}_8$ | 0.226 | 0.00541 |
| $\text{Na}_2\text{S}_2\text{O}_8$ | 0.125 | 0.00577 |
| $\text{Na}_2\text{S}_2\text{O}_8$ | 0.127 | 0.00533 |
| $\text{K}_2\text{S}_2\text{O}_8$ | 0.108 | 0.00545 |
| $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 0.229 | 0.0061 |

The curve for the ammonium salt showed rather more irregularity than the others, and its mean velocity-coefficient was, as shown, appreciably higher. This is perhaps explained by the formation of traces of nitric acid by oxidation, with consequent acceleration, but the divergence from the normal course is only slight.

Experiments with sodium persulphate solution containing added sodium nitrate (selected as a typical neutral salt of the same metal) have proved that the only effect of such addition is to raise slightly the unimolecular constant. Thus, in a test with 0.1283-sodium persulphate and 0.25-sodium nitrate solution, with twelve experimental

points covering a range of 85 per cent. decomposition, k_1 was found to vary irregularly between the extreme values 0.0062 and 0.0068, with a mean value of 0.0065. On the other hand, it will be shown that acids largely accelerate the action, and the special influences of added sulphates will also be dealt with later.

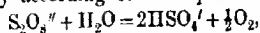
The magnesium salt, in contrast to those of the alkali metals, shows distinctly the effect of auto-acceleration, which, in this case, is probably to be explained by the formation of some non-ionised magnesium sulphate and free hydrogen ions, according to the equation:



Thus, in an experiment in which the initial concentration of magnesium persulphate was 0.2414, the unimolecular coefficient, calculated in the usual way, was found to increase steadily from about 0.0055 (appreciably equal to that of the sodium or potassium salt) at the start to 0.0066 when the action was half completed, and 0.0092 when less than 10 per cent. remained undecomposed. A similar, but much more pronounced, auto-acceleration will be shown to occur in the case of the barium salt, where the precipitation of the insoluble sulphate necessarily adds hydrogen ions to the solution. But the case of persulphuric acid itself must be discussed first.

Class II.—Persulphuric Acid.

In this case the curves obtained are again of the simple unimolecular form, with no sign of acceleration by increase of hydrogen ions; but it differs in two respects from that of the persulphates of the alkali metals. In the first place, the velocity is considerably greater, and, in the second place, the value of its coefficient is dependent on the initial concentration, so as to vary in different experiments while constant in any one. These facts are in accordance with the hypothesis already put forward, that the action proceeds practically according to the equation:



and that it is accelerated by the hydrogen ions which are initially present and remain unchanged in concentration. Such a hypothesis leads to the differential equation:

$$\frac{dx}{dt} = (k_2 + kA)(A - x),$$

where $k_2 + kA$ is necessarily a constant (K) in any given experiment, and

$$K = k_2 + kA = \frac{1}{t_2 - t_1} \log_e \frac{A - x_1}{A - x_2}$$

A simple explanation suggests itself for this accelerative action

of hydrogen ions. It may be assumed that, at the dilutions employed, the great bulk of the persulphuric acid is completely ionised into 2H^+ and $\text{S}_2\text{O}_8^{''}$, while a small proportion is converted into H^+ and $\text{HS}_2\text{O}_8'$. If this proportion be small enough, the total H^+ concentration may be taken as constant and equal to $2A$, whilst that of the $\text{S}_2\text{O}_8^{''}$ is appreciably equal to $A-x$, and that of the $\text{HS}_2\text{O}_8'$ itself is therefore proportional to $A(A-x)$. If, further, the $\text{HS}_2\text{O}_8'$ has a sufficiently high rate of reaction as compared with the $\text{S}_2\text{O}_8^{''}$, it will make itself felt in spite of its small concentration, and the total velocity of the action will be the sum of two velocities, $k_2(A-x)$ and $kA(A-x)$, in accordance with the equation already given.

By comparison of experiments with different A values, it is easy to evaluate k_2 and k ; and it has been found in this way that $k_2=0\cdot010$ and $k=0\cdot163$. These figures are illustrated by a comparison of the found and calculated velocity coefficients in table II. The fact that k_2 is nearly twice as great as the k , of sodium or potassium persulphate is difficult to explain on any hypothesis, for it implies some influence of the hydrogen ions other than that represented by the term $kA(A-x)$ and independent of their concentration. It is a fact, however, that, whilst $dx/dt=0\cdot0055(A-x)$ holds for the sodium and potassium salts, the equation for persulphuric acid is

$$\frac{dx}{dt}=(0\cdot010+0\cdot163A)(A-x)=K(A-x).$$

TABLE II.

Persulphuric Acid.

| A . | K (found). | K (calculated). |
|--------|--------------|-------------------|
| 0.2526 | 0.0527 | 0.0518 |
| 0.1251 | 0.0304 | 0.0304 |
| 0.1237 | 0.0302 | 0.0302 |
| 0.0923 | 0.0258 | 0.0250 |
| 0.0644 | 0.0210 | 0.0205 |
| 0.0416 | 0.0184 | 0.0168 |

The solutions used in the first, third, and fourth of these tests were prepared from barium persulphate by adding the calculated quantity of sulphuric acid, and were filtered from the barium sulphate; while those used in the second, fifth, and sixth were obtained by allowing barium persulphate solution to decompose automatically at 80° , and contained the precipitated sulphate in suspension. These cases will be discussed later.

Persulphuric Acid with Added Nitric Acid.

In this case there is a permanent increase of the hydrogen ions, and, if the initial concentrations of the two acids (both reckoned as dibasic, that is, as $\text{H}_2\text{S}_2\text{O}_8$ and $\text{H}_2\text{N}_2\text{O}_8$) be respectively A and B , the course of the action should be expressed by the equation:

$$\frac{dx}{dt} = \{k_2 + k(A+B)\}(A-x),$$

where $k_2 + k(A+B)$ appears as a unimolecular constant in any given experiment, and

$$K = k_2 + k(A+B) = \frac{1}{t_2 - t_1} \log_e \frac{A - x_1}{A - x_2}.$$

This was confirmed by the experiments summarised in table III. The first of these tests was made with an original mixture of persulphuric acid and nitric acid, while the other three were the later parts of experiments, in which barium persulphate, mixed with nitric acid, was allowed to decompose at 80° until there remained only persulphuric acid and nitric acid in solution, and the subsequent decomposition was then studied. These tests will be referred to later. The figures in the last column of the table show the value which K would have if the nitric acid were absent (compare table II), and are given to indicate clearly its effect.

TABLE III.

Persulphuric Acid with Added Nitric Acid.

| A . | B . | K (found). | K (calculated). | K' (original). |
|--------|--------|--------------|-------------------|------------------|
| 0.1248 | 0.1212 | 0.0500 | 0.0508 | 0.0304 |
| 0.0635 | 0.1845 | 0.0508 | 0.0504 | 0.0204 |
| 0.0628 | 0.1255 | 0.0414 | 0.0407 | 0.0202 |
| 0.0630 | 0.0634 | 0.0315 | 0.0306 | 0.0203 |

Mixed Persulphuric Acid and Sodium Persulphate.

The theory for such a case may be given on the assumption that the k_1 and k_2 constants are active approximately in proportion to the unchanging relative quantities of Na^+ and H^+ , and that the latter also contributes its special accelerative effect. Thus, if the initial $\text{H}_2\text{S}_2\text{O}_8$ be A , and the initial $\text{Na}_2\text{S}_2\text{O}_8$ be B , whilst x represents the total S_2O_8 destroyed, A and B will also represent at any time the $-(\text{H}^+)_2$ and the $(\text{Na}^+)_2$ respectively, and

$$\frac{dx}{dt} = \{k_2 \frac{A}{A+B} + k_1 \frac{B}{A+B} + kA\}(A+B-x).$$

In any given experiment therefore a unimolecular constant should be obtained, and

$$K = k_2 \frac{A}{A+B} + k_1 \frac{B}{A+B} + kA = \frac{1}{t_2 - t_1} \log \frac{A+B-\alpha_1}{A+B-\alpha_2}$$

In one test, in which $A=0.1285$ and $B=0.1234$, a mean value of 0.0276 was found for K in place of the calculated value 0.0288. In another, in which $A=0.0625$ and $B=0.1250$, the found and calculated values were respectively 0.0183 and 0.0172. The agreement is thus fairly satisfactory in both cases.

Persulphuric Acid with Added Sodium Nitrate.

This case is similar to the last, except that, the permanent concentrations of the $(H')_2$ and $(Na')_2$ being respectively A and B , that of the S_2O_8'' at any time is $A-x$ instead of $A+B-x$. The constant is here therefore

$$K = k_2 \frac{A}{A+B} + k_1 \frac{B}{A+B} + kA = \frac{1}{t_2 - t_1} \log \frac{A-\alpha_1}{A-\alpha_2}$$

In the only test carried out, $A=0.1377$ and $B=0.0625$, giving the calculated value of the constant as 0.0311. The mean experimental value was 0.0325, which is identical with that calculated on the assumption that the sodium nitrate is quite without effect. The difference is in any case too small to be significant, but it may be pointed out that a similar discrepancy was exhibited by the mixture of sodium persulphate and sodium nitrate, indicating that the latter has a small accelerative effect, not included in the theory, which may, in the present case, compensate for the expected small lowering of the K value.

Class III.—Barium Persulphate.

This case differs from the others in the precipitation of the product barium sulphate, and it differs also in the form of the curve in which x is plotted against t ; for this, being at first concave towards the x axis, at once points to strong auto-acceleration. The total change affecting the barium salt is represented by the equation :



and it must occur in two steps, namely :

- (1) $S_2O_8'' + H_2O = 2HSO_4' + \frac{1}{2}O_2$,
- (2) $2Ba'' + 2HSO_4' = 2BaSO_4 + 2H^+$.

The first of these is a relatively slow action, and the second keeps pace with it. Thus $2Ba''$ disappear from the solution for $\text{one } S_2O_8''$ destroyed; and if the latter be x , as in previous cases, it is evident that x also represents the persulphuric acid (or acidity) produced, and $A-2x$ represents the barium persulphate remaining.

This holds until $A - x = x = \frac{1}{2}A$, when the precipitation of the barium is complete, and subsequent action is concerned only with persulphuric acid. The whole action may thus be divided into two consecutive stages, the characters of which are shown in the following summary:

| | Total S_2O_8 | BaS_2O_8 | $H_2S_2O_8$ | Form of curve. |
|----------------|----------------------------|------------|----------------|---------------------|
| First stage | $A - x$ | $A - 2x$ | x | Autocatalytic |
| Half-way point | $x = \frac{1}{2}A = A - x$ | 0 | $\frac{1}{2}A$ | — |
| Second stage | $A - x$ | 0 | $A - x$ | Simple unimolecular |

Three of the six experiments with persulphuric acid solutions summarised in table II were, in fact, the second stages of experiments with barium persulphate, which will now be dealt with in greater detail. Comparison of these with the others shows that the presence of precipitated barium sulphate (since there was no other real difference) does not appreciably affect the velocity of persulphate decomposition by any kind of contact catalysis. A similar conclusion may be drawn from the sodium persulphate solutions of table I, one of which (the third) was mixed with the precipitate beforehand in order to test this question. It may therefore be concluded safely that the formation of this product has no such direct effect on the decomposition of barium persulphate itself in the first stage of the action.

In table II, which referred only to persulphuric acid, A and x were given the corresponding significance, and were equal respectively to $\frac{1}{2}A$ and $x = \frac{1}{2}A$, where the symbols are used in reference to the original barium persulphate contents, as in the above summary. But they must now be used in this latter sense, and the equation for the curve, after the complete precipitation of the barium, must be written $dx/dt = (k_2 + kA/2)(A - x)$.

Now, since the whole curve is continuous, it is evident that the equation for the first, or autocatalytic, stage must be such as to become identical with that just given at the half-way point, where $x = \frac{1}{2}A$. But it has been shown already that the k_2 of persulphuric acid and the k_1 of sodium or potassium persulphates have very different values, so that it might fairly be expected that the constant (k_3) for barium persulphate should differ from k_2 , and perhaps also from k_1 . Such proves to be the case, for it can be shown by a graphic method that the initial velocity of the decomposition of the pure barium salt solution, when it is as yet unmixed with persulphuric acid (when $x=0$), approximates to $dx/dt = 0.0040A$. We thus have $k_3 = 0.0040$, whilst $k_1 = 0.0035$ and $k_2 = 0.010$, and the catalytic constant $k = 0.163$. It must therefore be assumed that, in any mixture of two of these salts, the appropriate constants will be operative in proportion to

the amounts present, and that, consequently, the equation for the first stage of the barium persulphate action is:

$$\frac{dx}{dt} = (k_3 \frac{A-2x}{A-x} + k_2 \frac{x}{A-x} + kx)(A-x).$$

This conforms to the requirements, for the contents of the first bracket are equal to k_3 at the starting point, where $x=0$, and to $k_2 + kA/2$ at the half-way point, where $x=A/2$. It will be shown, also, that it expresses the whole of the experimental results with considerable accuracy. It is, perhaps, not superfluous to point out that, if hydrogen and barium persulphates had the same velocity constant (if $k_3=k_2$), the equation would be the ordinary one expressing an autocatalysed unimolecular action, for it would then become $dx/dt = (k_2 + kx)(A-x)$.

By integration of the above differential equation, we obtain an equation which may be written:

$$k(M+N) = \frac{1}{t} \log_e \frac{M(N+x)}{N(M-x)}$$

where M and N are constants in any given experiment, but vary with the initial concentration, and have the values:

$$M = \sqrt{\left(\frac{A}{2} + \frac{k_2 - 2k_3}{2k}\right)^2 + \frac{k_3 A}{k}} + \left(\frac{A}{2} + \frac{k_2 - 2k_3}{2k}\right)$$

$$N = \sqrt{\left(\frac{A}{2} + \frac{k_2 - 2k_3}{2k}\right)^2 + \frac{k_3 A}{k}} - \left(\frac{A}{2} + \frac{k_2 - 2k_3}{2k}\right).$$

Such an equation is of but little use for theoretical purposes unless M and N can be evaluated by independent measurements of the fundamental constants from which they are derived; but we are able to do this in the present case, having found already k_2 and k from the study of persulphuric acid, and k_3 from the initial velocity of pure barium persulphate solutions. We are thus enabled to compare the results calculated from the integrated equation with those obtained by experiment.

The details of one complete experiment with initially neutral barium persulphate solution are shown in table IV. The values of M and N , given at the head of the table, were calculated from those of A , k , k_2 , and k_3 ; and the theory of the first stage of the action may be tested by the constancy of $\frac{1}{t} \log_e \frac{M(N+x)}{N(M-x)}$ at different values of t , and also by its agreement with the calculated value of $0.4343k(M+N)$. Also the time is noted (as read from the curve) at which $x=\frac{1}{2}A$, that is, the time of the complete precipitation of the barium sulphate. The simple unimolecular character of the decomposition of the persulphuric acid in the second

stage is shown by the practical constancy of the normal logarithmic function, calculated from the observed values of x and t , and the theory of its dependence on A by a comparison of its mean value with that of $k_2 + kA/2$ (compare table II).

TABLE IV.

Barium Persulphate. $A=0.2502$.

First Stage. $M=0.2840, N=0.0216$.

| t | x | $1/t \log_{10} \frac{M(N+x)}{N(M-x)}$ |
|-----|--------|---------------------------------------|
| 10° | 0.0131 | 0.0226 |
| 25 | 0.0398 | 0.0208 |
| 35 | 0.0663 | 0.0207 |
| 45 | 0.0974 | 0.0205 |
| 50 | 0.1160 | 0.0206 |

Mean constant found = 0.0210.

Calculated value of $0.4343 k(M+N)$ = 0.0216.

Second Stage, after complete precipitation of Ba at $t=52.5^\circ$.

| t | x | $1/t - 60 \log_{10} \frac{A - 0.1558}{A - x}$ |
|-----|--------|---|
| 60° | 0.1558 | — |
| 70 | 0.1796 | 0.0126 |
| 85 | 0.2068 | 0.0135 |
| 100 | 0.2221 | 0.0132 |
| 115 | 0.2336 | 0.0137 |
| 135 | 0.2411 | 0.0135 |
| 155 | 0.2441 | 0.0125 |

Mean constant found = 0.0132.

Calculated value of $0.4343(k_2 + kA/2)$ = 0.0132.

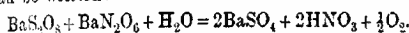
The details of two tests with smaller concentrations of barium persulphate may be given more briefly. In one of these the value of A was 0.1288, whence $0.4343k(M+N)=0.0128$ by calculation, and during the first stage of the action (sixty-five minutes) the values found for $\frac{1}{t} \log_{10} \frac{M(N+x)}{N(M-x)}$ ranged from 0.0130 to 0.0134 (mean = 0.0132). During the second stage of the same experiment, the mean unimolecular constant found was 0.0091 in place of the calculated value 0.0089. In the other case, A was 0.0832, whence $0.4343k(M+N)=0.0093$, and the constant found during the first stage (seventy minutes) ranged from 0.0103 to 0.0112 (mean, 0.0109), while the calculated and found unimolecular constants of the second stage were 0.0073 and 0.0080. In this case therefore the numerical agreement was not quite so good as in those of the stronger solutions.

It seems worth while to call attention here to a striking contrast

between the persulphate case and that of the decomposition of cyanates in aqueous solution, which in some respects is very similar (Masson and Masson, *loc. cit.*). Barium cyanate, which precipitates barium carbonate, gives a simple unimolecular curve, whilst the cyanates of sodium and potassium, which yield soluble ammonium carbonate, give strongly auto-accelerated unimolecular curves. Barium persulphate, which precipitates barium sulphate, gives strongly auto-accelerated unimolecular curves, whilst the persulphates of sodium and potassium, which yield soluble acid sulphates, give simple unimolecular curves. In the former case, it was proved that ammonium carbonate accelerates the action, whilst in the latter case soluble acid sulphates have no such influence, but their hydrogen ions have, when liberated by the precipitation of insoluble sulphate.

Mixed Barium Persulphate and Barium Nitrate.

If the latter be added in quantity equivalent to the former (or more), the barium ions cannot become exhausted by precipitation as barium sulphate so long as persulphate ions remain, and the whole action can be written:



The action therefore does not divide into two distinct stages as in the case of initially pure barium persulphate, but is marked throughout its course by continuous precipitation and increase of hydrogen ion concentration. Hence the auto-catalytic character must be also continuous, and this is found to be the case.

If A represent the initial concentration of the barium persulphate and B that of the barium nitrate, the composition of the solution at any subsequent time is such that it contains barium and hydrogen persulphates and nitrates with the following concentrations: $\text{S}_2\text{O}_8^{--} = A - x$, $(\text{NO}_3)_2 = B$, $\text{Ba}^{++} = A + B - 2x$, and $(\text{H}^+)_2 = x$. The total cations or anions (considered as bivalent) are thus always equal to $A + B - x$.

If, as in the case of initially pure barium persulphate, it be assumed that the barium and hydrogen ions are operative in proportion to their relative concentrations, while the latter also produces their special catalytic effect, we have the following differential equation to express the course of the action:

$$\frac{dx}{dt} = \frac{k_1}{k_2} \frac{A + B - 2x}{A + B - x} + k_2 \frac{x}{A + B - x} + kx(A - x),$$

which, by integration, gives:

$$k(M + N) = \frac{1}{t} \left\{ \frac{N + A + B}{N + A} \log_e \frac{A(N + x)}{N(A - x)} - \frac{M - A - B}{M - A} \log_e \frac{A(M - x)}{M(A - x)} \right\},$$

where M and N are constants in any given experiment, and have the values:

$$M = \sqrt{\left(\frac{A+B}{2} + \frac{k_2 - 2k_3}{2k}\right)^2 + \frac{k_3}{k}(A+B)} + \left(\frac{A+B}{2} + \frac{k_2 - 2k_3}{2k}\right),$$

$$N = \sqrt{\left(\frac{A+B}{2} + \frac{k_2 - 2k_3}{2k}\right)^2 + \frac{k_3}{k}(A+B)} - \left(\frac{A+B}{2} + \frac{k_2 - 2k_3}{2k}\right).$$

An obvious simplification of the formula results where, as in the actual experiment (table V), the barium persulphate and nitrate are given the same initial concentration, or $B=A$. The values of M and N given at the head of the table were calculated from that of A and those of k_3 , k_2 , and k , as already determined. In the third column are given the found values of the constant:

$$K = \frac{1}{t} \left\{ \frac{N+2A}{N+A} \log_{10} \frac{A(N+x)}{A(A-x)} - \frac{M-2A}{M-A} \log_{10} \frac{A(M-x)}{M(A-x)} \right\},$$

which may be compared with each other as to constancy and also with the calculated value of $0.4343k(M+N)$, given at the end of the table. The agreement is fairly satisfactory.

TABLE V.

Barium Persulphate and Barium Nitrate in Equimolecular Mixture.

$$B=A=0.1253. \quad M=0.2845. \quad N=0.0217.$$

| t . | x . | K . |
|-------|--------|--------|
| 10" | 0.0062 | 0.0240 |
| 20 | 0.0147 | 0.0255 |
| 30 | 0.0223 | 0.0230 |
| 45 | 0.0355 | 0.0223 |
| 60 | 0.0457 | 0.0208 |
| 70 | 0.0577 | 0.0229 |
| 75 | 0.0643 | 0.0219 |
| 90 | 0.0791 | 0.0220 |
| 105 | 0.0928 | 0.0223 |
| 120 | 0.1019 | 0.0220 |
| 135 | 0.1105 | 0.0223 |
| 160 | 0.1200 | 0.0238 |
| 195 | 0.1236 | 0.0233 |

Mean value of K found = 0.0229.

Calculated value of $0.4343k(M+N)$ = 0.0217.

Barium Persulphate with Added Nitric Acid.

Here, as in the case of pure barium persulphate, the action may be expected to divide itself into two stages, since the barium must be totally precipitated when $x=A-x=\frac{1}{2}A$. If B stand for the added nitric acid (reckoned as dibasic) or for the initial $(H^+)_{\text{D}}$, the quantity of the latter must steadily increase by production of persulphuric acid during the first stage, where its value is $B+x$; but from the middle point onwards through the second stage it

must retain the value $B + \frac{1}{2}A$. As in the simple case, the Ba^{++} must have the value $A - 2x$ until this becomes nil at the middle point, whilst the $\text{S}_2\text{O}_8^{--}$ must have the value $A - x$ from first to last. The first stage should therefore show an autocatalytic curve merging into the simple unimolecular one of the second stage, and the respective differential equations should be:

$$(I.) \quad \frac{dx}{dt} = \{k_3 \frac{A - 2x}{A + B - x} + k_2 \frac{B + x}{A + B - x} + k(B + x)\}(A - x),$$

$$(II.) \quad \frac{dx}{dt} = \{k_2 + k(B + \frac{1}{2}A)\}(A - x),$$

which are identical when $x = \frac{1}{2}A$.

These equations, indeed, follow logically from those already confirmed for the case of a mixture of barium persulphate and barium nitrate, for it is obvious that such a mixture, if it initially contains excess of the former ingredient, must, at a certain point in its history, become converted into a solution of barium persulphate and nitric acid, and subsequently into one of persulphuric acid and nitric acid. There are thus three distinct stages in such an action, and it seems an unavoidable conclusion that the theory which is quantitatively applicable to the mixtures of the first stage (table V) and also to those of the third (table III) must apply equally well to those of the second. Nevertheless, it has been found in a series of experiments with barium persulphate and nitric acid in different proportions that the nitric acid produces initially only about half the acceleration indicated in equation I, although it gradually increases its effect as the action proceeds, and attains full value as an accelerator when the barium is completely precipitated, after which equation II holds well. Without further investigation, it does not seem possible to reconcile these observations.

The Influence of Sulphates, Produced or Added.

As already pointed out, sulphuric acid or acid sulphate is a necessary product of the decomposition of persulphuric acid or persulphates of the sodium class of metals, and yet there is in these cases an entire absence of that autocatalysis which is so marked a feature in the case of barium persulphate, where the growing acidity is due to persulphuric acid formed by the precipitation of barium sulphate. The explanation already suggested is that the negative ions produced are in reality HSO_4^- (not SO_4^{--}), so that there is no appreciable increase in the concentration of H^+ ions (the true accelerator) unless the conditions are disturbed by precipitation or, to a smaller extent, by the process mentioned in the

case of the magnesium salt. Briefly, the hypothesis is that sulphuric acid acts practically as a monobasic acid in these solutions, while persulphuric acid itself acts as a dibasic one.

The most direct test of this view, apart from the evidence already given in support of it, is obtained by studying the velocity of the decomposition of persulphuric acid and sodium persulphate solutions, to which have been added beforehand known quantities of sulphuric acid, sodium hydrogen sulphate (that is, sodium sulphate and sulphuric acid), or sodium sulphate. According to the hypothesis, the velocity coefficient should not be affected by adding either sodium sulphate or sodium hydrogen sulphate to sodium persulphate; sodium hydrogen sulphate should produce but a slight lowering of the coefficient of persulphuric acid by adding Na^+ ions to the solution without altering the H^+ concentration; sodium sulphate should largely reduce this coefficient by converting free H^+ into HSO_4^- ; and added sulphuric acid should accelerate in both cases, but only to the extent due to it as a monobasic acid, or half as much as the equivalent quantity of nitric acid or of persulphuric acid itself. In all cases the numerical results predicted by the hypothesis can be calculated from a knowledge of the fundamental constants already given, namely, $k_1 = 0.0055$ for $(\text{Na}^+)_2$, $k_2 = 0.010$ for $(\text{H}^+)_2$, and $k = 0.163$ for $(\text{H}^+)_2$ acceleration.

The results of the experiments performed confirm these expectations, with one rather notable exception in the case of the addition of sodium sulphate to sodium persulphate. Here the unimolecular constant, although it has at first the normal and expected value of about 0.0055, quickly diminishes until it reaches a steady value, considerably smaller and dependent on the amount of added neutral sulphate. Four tests were made with approximately $\frac{1}{8}$ -molar-sodium persulphate, containing respectively 0.060, 0.125, 0.128, and 0.255 molecule of sodium sulphate. In each case the curve showed a similar retardation until about one-fifth of the persulphate was decomposed, and thereafter, and reckoned from this point, a good unimolecular constant was obtained, the respective values being 0.0035, 0.0025, 0.0025, and 0.0020. These results point to some complication, which, as will be shown, is never met with except in the presence of mixed neutral and acid sulphate, and which is perhaps due to a reverse action in which the dissolved oxygen plays a part; for this product is the only substance present whose quantity is initially nil, and tends, on account of its limited solubility, to increase quickly to a maximum.

In all the other cases the curves showed steady unimolecular actions, and the found velocity coefficients agreed fairly well with those calculated in accordance with the hypothesis. Although the

agreement is not quantitatively exact, it is noteworthy that the results fully establish the following facts:

(1) Addition of sodium hydrogen sulphate produces no marked acceleration, showing that it does not add H^+ ions; (2) addition of sodium sulphate to persulphuric acid produces a large retardation, which points to a suppression of H^+ ions; (3) addition of sulphuric acid produces such acceleration as points to the ionisation of about half its hydrogen.

The results are summarised in table VI. In the first column are given the nature and concentration of the persulphate used. In the second, the added sulphate is similarly specified. In the third, under K (found), is given the experimental unimolecular constant, this being, as in previous cases, the mean of several concordant values found over a large range of action. In the fourth column, under

K (calculated), is given the value of $k_1 \frac{Na^+}{Na^+ + H^+} + k_2 \frac{H^+}{Na^+ + H^+} + k(H^+)^2$,

where the ionic symbols refer to the corresponding concentrations after allowance for the conversion of all SO_4 into HSO_4' ions. In the fifth column, under K (original), is given, for comparison, the value the constant would have if the added sulphate produced no effect whatever.

TABLE VI.
The Effects of Added Sulphates.

| Persulphate. | Sulphate. | K found. | K calculated. | K original. |
|---------------------|-------------------|---------------|--------------------|------------------|
| 0.1285 $Na_2S_2O_8$ | 0.1338 $NaHSO_4$ | 0.0060 | 0.0055 | 0.0055 |
| 0.1304 $Na_2S_2O_8$ | 0.1332 H_2SO_4 | 0.0161 | 0.0179 | 0.0055 |
| 0.1273 $Na_2S_2O_8$ | 0.3767 H_2SO_4 | 0.0372 | 0.0389 | 0.0055 |
| 0.1183 $H_2S_2O_8$ | 0.1250 Na_2SO_4 | 0.0151 | 0.0160 | 0.0293 |
| 0.1245 $H_2S_2O_8$ | 0.1366 $NaHSO_4$ | 0.0304 | 0.0288 | 0.0303 |
| 0.1235 $H_2S_2O_8$ | 0.0508 H_2SO_4 | 0.0370 | 0.0343 | 0.0301 |
| 0.1275 $H_2S_2O_8$ | 0.1194 H_2SO_4 | 0.0421 | 0.0405 | 0.0308 |
| 0.1285 $H_2S_2O_8$ | 0.1544 H_2SO_4 | 0.0425 | 0.0435 | 0.0309 |

The Effects of Added Alkali.

Levi and Migliorini found that alkalis accelerate the persulphate decomposition, but to a smaller extent than acids. Our experiments, however, with persulphates of the first class do not confirm this. When sodium or potassium persulphate is mixed with the corresponding alkali in equivalent, or greater, amount, a regular unimolecular curve is obtained with a constant which is almost identical with that characteristic of the pure salt solution. It is, indeed, very slightly smaller, which is probably accounted for by the physical effect of the extra dissolved substance, but there is no evidence of positive or negative acceleration by hydroxyl ions. These, of course, become destroyed as the action proceeds, for they

necessarily neutralise the acid sulphate product, and any such catalytic effect would thus continuously diminish, and the curve would not be that of a simple unimolecular action. It is noteworthy that the normal sulphate which results from this neutralisation does not produce any such marked retardation as was observed when the same salt was added beforehand to sodium persulphate, so that it may be concluded that the reaction responsible for that complication can occur only in the presence of both normal and acid sulphate, as already mentioned.

The results of four experiments are summarised in table VII. The k_1 values here may be compared with those cited for the pure salts in table I.

TABLE VII.
Effects of Added Alkali.

| Persulphate. | Alkali. | k_1 found. |
|---|------------|--------------|
| 0.1192Na ₂ S ₂ O ₈ | 0.2192NaOH | 0.0051 |
| 0.1185Na ₂ S ₂ O ₈ | 0.2236NaOH | 0.0051 |
| 0.1214Na ₂ S ₂ O ₈ | 0.3434NaOH | 0.0049 |
| 0.0797K ₂ S ₂ O ₈ | 0.2040KOH | 0.0050 |

The behaviour of barium persulphate when mixed with barium hydroxide is quite different, and is difficult to reconcile with any general theory. The autocatalytic curve of the pure salt solution has been fully explained by the production of persulphuric acid, but here it is evident that neutralisation must occur continuously, and that the precipitation of barium sulphate is accompanied by a progressive diminution of alkali instead of an increase of acidity. Indeed, the course of the action is followed in practice by alkalimetry instead of the usual acidimetry. Now, as it has been proved that hydroxyl ions exert no appreciable catalytic effect in the case of the salts of the alkali metals, it seems inevitable that barium persulphate, when mixed with sufficient barium hydroxide, should give a continuous simple unimolecular curve with its own velocity constant (k_3). Nevertheless, the curves obtained show a much higher initial velocity than corresponds with k_3 , that is, an initial acceleration by the added alkali, and they also give evidence of a further acceleration as the alkali subsequently diminishes. We are unable to explain these facts.

The Temperature Effect.

Experiments were made with sodium persulphate and with persulphuric acid at 70° and 90° for comparison with those at 80° already described. The mean values of the unimolecular coefficients are given in the following table. In the case of persulphuric acid, it must be remembered that this coefficient is largely dependent on

the initial concentration (A), for it has been shown to be the sum of two terms, $k_2 + kA$, whereas in the case of the salt it is a simple constant, k_1 . It appears, however, that the constants at 90° are all about tenfold those at 70° .

TABLE VIII.
The Temperature Effect.

| Salt. | A . | Unimolecular coefficients. | Temperature. |
|-----------------------------------|-------|----------------------------|--------------|
| $\text{Na}_2\text{S}_2\text{O}_8$ | 0.125 | 0.0016 | 70° |
| $\text{Na}_2\text{S}_2\text{O}_5$ | 0.126 | 0.0055 | 80 |
| $\text{Na}_2\text{S}_2\text{O}_8$ | 0.130 | 0.0161 | 90 |
| $\text{H}_2\text{S}_2\text{O}_8$ | 0.124 | 0.0111 | 70 |
| $\text{H}_2\text{S}_2\text{O}_5$ | 0.124 | 0.0302 | 80 |
| $\text{H}_2\text{S}_2\text{O}_8$ | 0.116 | 0.1035 | 90 |

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CCXX.—A Simple Method of Preparing Tetranitromethane.

By FREDERICK DANIEL CHATAWAY.

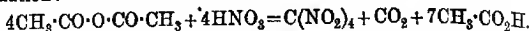
TETRANITROMETHANE can easily* be obtained without danger, and in almost theoretical amount, by allowing equal molecular amounts of nitric acid † and acetic anhydride to interact ‡ at the ordinary temperature for several days. Some heat is developed on mixing, and slight cooling is necessary during this part of the process, otherwise the action may become so vigorous that loss of material results, but, so far as the author's experience goes, it never becomes explosive in character.

* The methods hitherto described for the preparation of tetranitromethane, namely, (1) nitrating nitroform (Schischkoff, *Annalen*, 1861, 119, 247), (2) the action of diacetylorthonitric acid on acetic anhydride (Pictet and Guequand, *Ber.*, 1903, 36, 2225), (3) distilling nitrobenzene with a large excess of a mixture of nitric and sulphuric acids containing sulphur trioxide (Claesson, D.R.P. 1842291, and (4) adding acetic anhydride to a mixture of nitrogen pentoxide and nitrogen peroxide (Scheunck, D.R.P. 211198, 211199), leave much to be desired in the way of simplicity.

† The use of more than the equivalent amount of nitric acid is of no advantage; indeed, when an excess is added, the yield is seldom so good, as the acid ordinarily employed always contains some small amount of water.

‡ On the 7th of July, since this paper was written, the Farbenfabriken vorm. F. Bayer & Co. published a method (D.R.P. 224057) of preparing tetranitromethane exactly similar to that given above. As, however, this paper was read about a month earlier, namely, on June 18th (*Proc.*, 1910, 26, 164), and as many details not to be found in the specification are given, it seems desirable that it should be published in full.

The action takes place almost quantitatively according to the equation:



The tetranitromethane remains dissolved in the acetic acid, and separates out as a heavy, oily layer on pouring the product into water. Carbon dioxide is given off almost from the time of mixing, but the evolution is never rapid, and the tetranitromethane appears only to be formed gradually, as the yield is small unless the mixture is kept for some days.

When nitric acid attacks acetic anhydride, a mononitro-derivative is probably first produced, which is nitrated so much more readily than the parent compound that action proceeds until the three hydrogen atoms of a methyl group have been replaced. Hydrolysis then occurs, and the trinitroacetic acid formed slowly decomposes into carbon dioxide and nitroform, which as soon as it is liberated is converted by the remainder of the nitric acid into tetranitromethane.*

The operations necessary in this method are so simple and so easily carried out that the preparation is well adapted to take its place in any elementary course of practical organic chemistry to illustrate the ease with which aliphatic compounds can be nitrated, whilst the materials employed are so cheap and the yield is so satisfactory as to make tetranitromethane, which has hitherto been a somewhat unfamiliar substance, one of the most easily procurable of organic compounds.

Preparation of Tetranitromethane.

Thirty-one grams of nitric acid * (D^{15} 1.53) are placed in a 250 c.c. flask, and 50 grams of acetic anhydride are gradually added in quantities of about 2 c.c. at a time, the flask meanwhile being cooled in water, as some little heat is developed. If the flask is not cooled, action proceeds more and more vigorously as the temperature rises, and may, if unchecked, become violent. It is inadvisable therefore to allow the temperature to rise much above 20—25°.

When all the anhydride has been added, the flask is covered loosely by a watch-glass or inverted small beaker, and kept at the ordinary temperature for about a week. As the reaction proceeds, carbon dioxide is continuously but very slowly evolved, and the mixture, which at first is colourless, becomes brown, owing to the

* The anhydrous nitric acid required in the preparation is most easily obtained by slowly distilling ordinary fuming nitric acid from its own bulk of concentrated sulphuric acid; if ordinary concentrated nitric acid (D 1.41) is used, it is advisable to distil it twice from sulphuric acid. It is not necessary, although advisable if convenient, to distil off the acid under diminished pressure.

formation, in small quantity, of oxides of nitrogen. After a week, the tetranitromethane which remains dissolved in the acetic acid may be separated by pouring the mixture into about 150—200 c.c. of water. The bulk of the tetranitromethane subsides as a colourless, heavy, oily layer, which can be removed by means of a separating funnel, whilst a small quantity still remaining dissolved in the dilute acetic acid may easily be separated by means of a current of steam. The tetranitromethane passes over with the first few c.c. of the distillate, and separates as a heavy globule.

The tetranitromethane thus obtained may be freed from traces of acid by washing with water, or even better, although with slight loss, by distilling in a current of steam.* It is then separated and dried over fused calcium chloride.

Tetranitromethane as thus prepared is a heavy, very faintly yellow liquid. It can be distilled at 126° under the ordinary pressure, but the distillate is of a pale brown colour, due to oxides of nitrogen formed by some slight decomposition which takes place at this temperature, and still requires to be washed and dried to obtain it quite pure. If cooled a little below the ordinary temperature, it easily solidifies to a mass of colourless crystals.

The yield of tetranitromethane obtained is never quite the theoretical one, although by careful working it can be made to approximate to it. The small loss cannot be entirely, or even mainly, due to oxidation, as at no period of the action is there any considerable liberation of nitrous fumes; it is probably caused by some of the very heavy vapour being carried away in the escaping carbon dioxide, and lost during the processes of separation.

Using acid prepared as above, without removing the oxides of nitrogen,† the yield is approximately 80 per cent. of the theoretical, about 18—20 grams of pure, dry tetranitromethane being obtained from the weights of materials given.

It is immaterial whether the acetic anhydride be added to the nitric acid, or the nitric acid to the anhydride, but the former procedure is preferable, as the evolution of heat then occurs mainly during the first few additions of anhydride, which can be added more rapidly afterwards.

In a set of experiments to ascertain the rate of formation, a

* After distilling in a current of steam, the distillate containing the tetranitromethane as well as the residue is always bright yellow in colour, owing to the presence of dissolved nitroform, which is formed in small quantity when tetranitromethane is allowed to come into contact with water or is heated with it.

† There is no great advantage in freeing the anhydrous nitric acid from oxides of nitrogen, as even if the acid is completely colourless on mixing and the mixture is kept at 0° in a dry atmosphere it becomes coloured in a few days. The yield is slightly better if colourless anhydrous acid is employed, but the increased yield does not compensate for the extra labour involved in the preparation of the acid,

number of similar mixtures of the above quantities were made, and the amount of tetranitromethane formed was estimated after different intervals. After one day, 7.5 grams of tetranitromethane were obtained; after two days, 11.5 grams; after four days, 14.5 grams; after six days, 17 grams; and after eight days, 18.5 grams. After this, further keeping did not appreciably increase the yield.

The process can be accelerated by heating the mixed liquids cautiously until the action becomes sufficiently rapid to cause the temperature to rise even after removing the source of heat* and then checking the action by cooling; when this has been done several times, the liquid, which at first cannot be heated with safety much above 30°, may be heated to 80–100° without any violent action occurring, but on diluting the product the yield is not found to be anything like so good as when the mixture is simply allowed to remain at the ordinary temperature.

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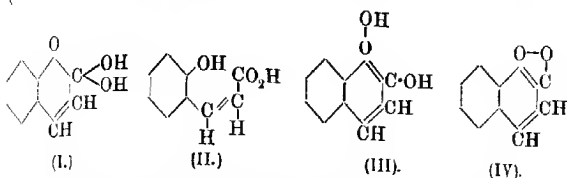
CCXXI.—*The Constitution of Coumarinic Acid.*

By ARTHUR CLAYTON.

WHEN coumarin is dissolved in aqueous sodium hydroxide, the sodium salt of coumarinic acid is produced, whereas the prolonged action of an alcoholic solution of the alkali results in the production of an alkali *o*-coumarate. Coumarinic acid has not yet been isolated, being resolved into coumarin and water at the moment of liberation from its salts, but its alkyl esters are known, these compounds being isomeric with the corresponding derivatives of *o*-coumaric acid. When the dialkyl esters of 3-nitrocoumarinic acid are boiled with aqueous alkalis, 3-nitrocoumarinic acid is produced from the acidified liquid, whereas the dimethyl ester of 3-nitro-*o*-coumaric acid under similar conditions yields the methyl ether of 3-nitro-*o*-coumaric acid (Miller and Kinkelin, *Ber.*, 1889, 22, 1708 *et seq.*). This difference of behaviour towards alkalis has been explained by Michael's formula (1) for coumarinic acid (*J. pr. Chem.*, 1888, [ii], 38, 27), which has also received support from Perkin (*Trans.*, 1881, 39, 560), Miller and Kinkelin (*Ber.*,

* If the mixture be heated until action becomes violent it is difficult to condense the products, torrents of brown fumes are evolved, and the quantity of tetranitromethane obtained is very small.

1889, 22, 1713), Roser (*Ber.*, 1882, 15, 2347), and Anschütz (*Annalen*, 1889, 254, 181):



On the other hand, the view has been held that coumarinic acid is the *cis*-isomeride (formula II) of *o*-coumaric acid. A third possible formula (III) is suggested by the constitution which Morgan and Micklethwait (*Trans.*, 1906, 89, 868) have proposed for coumarin (formula IV).

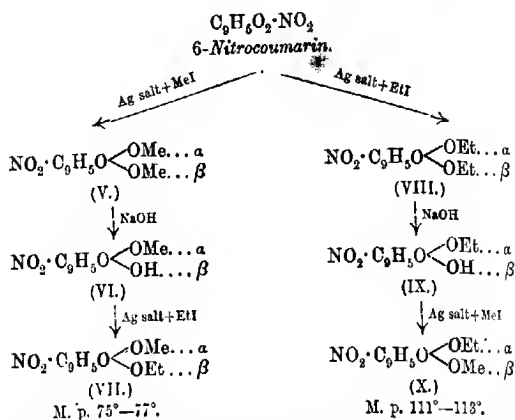
In order to confirm or exclude Michael's formula, the author of the present communication has investigated the alkyl derivatives of 5-nitrocoumarinic acid, the nitro-group being introduced in order to obtain solid compounds. It is obvious that if formula I represents the constitution of coumarinic acid, only one methyl ethyl ester could be prepared, whereas formulæ II and III indicate the possibility of the existence of two such derivatives. For convenience, the two hydroxyl groups will in this paper be distinguished by the letters α and β .

6-Nitrocoumarin dissolves in aqueous alkalis, and the solution, when treated with silver nitrate, yields *silver 5-nitrocoumarinate*. This salt, by interaction with methyl iodide, yields $\alpha\beta$ -dimethyl 5-nitrocoumarinate (V). The identity of this substance is established by boiling it with aqueous sodium hydroxide, 6-nitrocoumarin being readily regenerated. The $\alpha\beta$ -dimethyl 5-nitrocoumarinate is converted by partial hydrolysis into α -methyl 5-nitrocoumarinate (VI). The *silver* salt of the latter compound, when treated with ethyl iodide, yields α -methyl β -ethyl 5-nitrocoumarinate (VII).

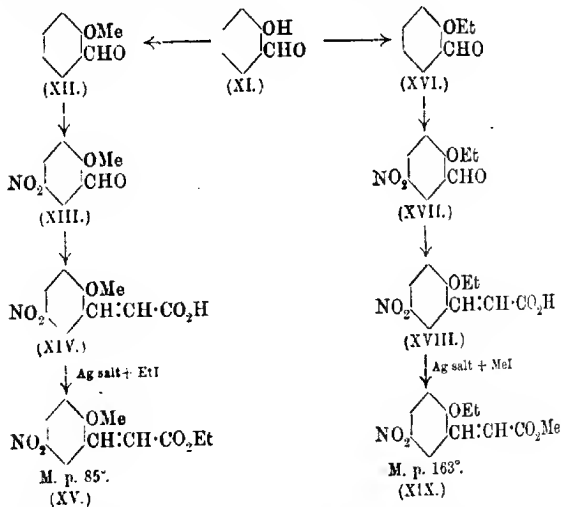
By a similar series of operations, $\alpha\beta$ -diethyl 5-nitrocoumarinate, α -ethyl 5-nitrocoumarinate, and β -methyl α -ethyl 5-nitrocoumarinate are obtained as indicated by formulæ VIII—X.

All the compounds V—X (p. 2104) are shown to be derivatives of 5-nitrocoumarinic acid by their exceedingly easy reversion to 6-nitrocoumarin when boiled with weak aqueous sodium hydroxide. α -Methyl β -ethyl 5-nitrocoumarinate and β -methyl α -ethyl 5-nitrocoumarinate proved to be distinctly different compounds, the former melting at 75—77°, and the latter at 111—113°, thus showing Michael's formula to be incorrect.

In order that the foregoing proof should not be invalidated by the possibility of one or both of the isomeric methyl ethyl esters



being derived from 5-nitrocoumaric acid by the rupture of the lactonic ring, an investigation of the ethers and esters of the latter acid was made as indicated by formulæ XI–XIX.



The methyl ether of 5-nitrocoumaric acid (XIV) was prepared according to Schnell's directions (*Ber.*, 1884, 17, 1382) as indicated by formulæ XI–XIV, and the silver salt of this acid heated with ethyl iodide, thus yielding the methyl ether of ethyl 5-nitro-

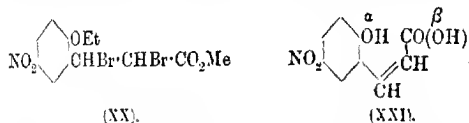
coumarinate (XV). By a similar series of reactions the *ethyl ether* of 5-nitrosalicylaldehyde, the *ethyl ether* of 5-nitrocoumaric acid, and the *ethyl ether* of methyl 5-nitrocoumarate are obtained (XVII–XIX).

The two methyl ethyl derivatives of 5-nitrocoumaric acid thus obtained proved to be distinctly different from the methyl ethyl derivatives of 5-nitrocoumarinic acid. The existence of these four isomeric methyl ethyl derivatives permanently excludes the possibility of Michael's formula being correct.

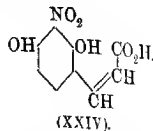
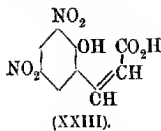
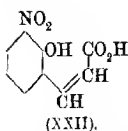
In order to ascertain which of the two remaining formulae represents the constitution of coumarinic acid, $\alpha\beta$ -dimethyl coumarinate and the *methyl ether* of methyl 5-nitrocoumarate were separately treated with bromine. In each case methyl $\alpha\beta$ -dibromo-5-nitro-2-methoxy- β -phenylpropionate was produced, thus excluding formula III.

Coumarinic acid is therefore proved to be the *cis*-isomeric of *o*-coumaric acid.

The positions occupied by the hydroxyl groups, which have been distinguished by the letters α and β , are indicated by treating the *ethyl ether* of methyl 5-nitrocoumarate, and β -methyl α -ethyl 5-nitrocoumarinate separately with bromine. Methyl $\alpha\beta$ -dibromo-5-nitro-2-ethoxy- β -phenylpropionate (XX) is produced in each case, thus showing that the α -group is phenolic, and that the β -group forms part of the carboxyl group (see formula XXI):



Formula II being established, the chemical behaviour of coumarinic acid can easily be explained. If a representation of the molecule be built up with suitable models, the side-chain is seen to follow approximately the sides of a regular hexagon, and the carboxyl group is brought into close proximity with the phenolic group (formula XXI), thus indicating the ready elimination of the elements of water. If, however, a nitro-group be introduced into position 3, the negative phenolic and nitro-groups exert a combined and powerfully repellent effect on the carboxyl group, which, being repelled from the immediate neighbourhood, no longer enters into chemical action with the phenolic group. This accounts for the fact that 3-nitrocoumarinic acid (XXII), 3:5-dinitrocoumarinic acid (XXIII), and 3-nitro-4-hydroxycoumarinic acid (XXIV) exist in the free state (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706; Clayton, this vol., p. 1390 *et seq.*):



The ease with which the alkyl ether esters of the coumarinic acids undergo complete hydrolysis is unusual, since phenyl ethers are generally not affected by aqueous alkalis. In all probability, however, after the removal of the alkyl from the carboxyl group, two causes operate in the second stage of the hydrolysis, namely, (1), the usual hydrolytic action of aqueous alkalis, and (2), that cause which effects the elimination of the elements of water from coumarinic acid itself. These two influences, acting concurrently, bring about the hydrolysis of the phenyl ether which aqueous alkalis alone are generally unable to effect.

Summary.

1. The two methyl ethyl ether-esters of 5-nitrocoumarinic acid and the two corresponding isomeric ether-esters of 5-nitrocoumaric acid have been prepared.
2. The two methyl ethers of methyl 5-nitrocoumarate and methyl 5-nitrocoumarinate yield the same bromine additive product when treated with bromine.
3. The above facts show that coumarinic acid is the *cis*-isomeride of o-coumaric acid. This view of the constitution of coumarinic acid affords a ready explanation of its chemical reactions.

EXPERIMENTAL.

The Ethers and Esters of 5-Nitrocoumarinic Acid.

6-Nitrocoumarin was found to be best prepared by dissolving coumarin in sulphuric acid (10 parts), and treating the solution with one molecular proportion of nitric acid (D 1.4) mixed with three times its volume of sulphuric acid, the temperature being kept below 20°. After one hour the solution is poured on crushed ice, and the precipitated solid crystallised from acetic acid.

Silver 5-nitrocoumarinate was obtained by dissolving 6-nitrocoumarin (10 grams) in an aqueous solution of sodium hydroxide (4.2 grams), and then adding a solution of silver nitrate (19 grams). The orange-red precipitate was washed with a little water and dried. When treated with dilute acids, the salt yields 6-nitrocoumarin:

0.2813 gave 0.1908 AgCl. $\text{Ag} = 51.04$.

$\text{C}_9\text{H}_5\text{O}_3\text{N}(\text{OAg})_2$ requires $\text{Ag} = 51.06$ per cent.

The Methyl Ether of Methyl 5-Nitrocoumarinate.—Silver 5-nitrocoumarinate (6 grams) was mixed with about 30 c.c. of ether, and then shaken with a mixture of methyl iodide (1.5 grams) and ether (10 c.c.) for one hour, the temperature rising during this operation. When cold, the contents were extracted with alcohol, from which solvent colourless needles, melting at 124–125°, were obtained:

0.1375 gave 0.2790 CO_2 and 0.0610 H_2O . $\text{C}=55.34$; $\text{H}=4.92$.

0.2146 „ 11.3 c.c. N_2 at 24° and 770 mm. $\text{N}=5.99$.

$\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}$ requires $\text{C}=55.70$; $\text{H}=4.64$; $\text{N}=5.91$ per cent.

The Ethyl Ether of Ethyl 5-Nitrocoumarinate.—Silver 5-nitrocoumarinate (10 grams) was treated with ethyl iodide (4 grams) in ethereal solution in the manner described in the preceding experiment, and the product extracted with alcohol. Colourless needles, melting at 104–105°, were obtained:

0.1404 gave 0.3020 CO_2 and 0.0740 H_2O . $\text{C}=58.66$; $\text{H}=5.85$.

0.2376 „ 11.7 c.c. N_2 at 25° and 750 mm. $\text{N}=5.41$.

$\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C}=58.87$; $\text{H}=5.66$; $\text{N}=5.28$ per cent.

The Methyl Ether of 5-Nitrocoumarinic Acid.—The methyl ether of methyl 5-nitrocoumarinate (6 grams) was dissolved in dilute alcohol, and heated to 100° with aqueous sodium hydroxide (1 gram) for about thirty minutes, when a portion of the liquid produced no turbidity on dilution with water. The mixture was then acidified with dilute hydrochloric acid, and the voluminous precipitate crystallised from alcohol or dilute acetic acid. Colourless needles were obtained, melting at 202–203°:

0.1647 gave 0.3230 CO_2 and 0.0650 H_2O . $\text{C}=53.48$; $\text{H}=4.39$.

0.1706 „ 10.1 c.c. N_2 at 26° and 754 mm. $\text{N}=6.52$.

$\text{C}_{10}\text{H}_9\text{O}_3\text{N}$ requires $\text{C}=53.81$; $\text{H}=4.04$; $\text{N}=6.28$ per cent.

The Ethyl Ether of 5-Nitrocoumarinic Acid.—This substance was obtained by the interaction of the ethyl ether of ethyl 5-nitrocoumarinate (6.5 grams) and sodium hydroxide (1 gram) in weak alcoholic solution, in the manner described in the preceding experiment. Colourless needles were produced, melting at 171–172°:

0.1498 gave 0.3080 CO_2 and 0.0662 H_2O . $\text{C}=56.07$; $\text{H}=4.94$.

0.1442 „ 8.0 c.c. N_2 at 25° and 754 mm. $\text{N}=6.14$.

$\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}$ requires $\text{C}=55.70$; $\text{H}=4.64$; $\text{N}=5.91$ per cent.

The Methyl Ether of Silver 5-Nitrocoumarinate.—The methyl ether of 5-nitrocoumarinic acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1.8 grams), and the yellow silver salt was precipitated as an almost colourless powder:

0.3100 gave 0.1004 Ag. $\text{Ag}=32.39$.

$\text{C}_{10}\text{H}_9\text{O}_3\text{NAg}$ requires $\text{Ag}=32.73$ per cent.

The Ethyl Ether of Silver 5-Nitrocoumarinate.—The ethyl ether of 5-nitrocoumarinic acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1.7 grams). An aqueous solution of silver nitrate (8 grams) was then added. The salt forms an almost colourless powder:

0.3116 gave 0.0980 Ag. Ag=31.45.

$C_{12}H_{10}O_5NaAg$ requires Ag=31.40 per cent.

The Methyl Ether of Ethyl 5-Nitrocoumarinate.—The methyl ether of silver 5-nitrocoumarinate (10 grams) was heated with ethyl iodide (5 grams) and a little ether for one hour at 100°. The product, when extracted with alcohol, yielded colourless needles, melting at 75–77°:

0.1178 gave 0.2462 CO_2 and 0.0580 H_2O . C=57.00; H=5.47.

0.1092 „ 5.7 c.c. N_2 at 24° and 756 mm. N=5.82.

$C_{12}H_{13}O_5N$ requires C=57.37; H=5.18; N=5.58 per cent.

The Ethyl Ether of Methyl 5-Nitrocoumarinate.—The ethyl ether of silver 5-nitrocoumarinate (10 grams) was mixed with ether and methyl iodide (5 grams), and subjected to the treatment described in the preceding experiment. The alcoholic extract yielded colourless needles, melting at 111–113°:

0.1594 gave 0.3328 CO_2 and 0.0744 H_2O . C=57.00; H=5.19.

0.1192 „ 6.4 c.c. N_2 at 24° and 756 mm. N=5.98.

$C_{12}H_{13}O_5N$ requires C=57.37; H=5.18; N=5.58 per cent.

The Ethers and Esters of 5-Nitrocoumaric Acid.

The Methyl Ether of Silver 5-Nitrocoumarate.—The methyl ether of 5-nitrocoumaric acid (1.6 grams), prepared according to Schnell's directions (*Ber.*, 1884, 17, 1382), was dissolved in a solution of sodium hydroxide (0.29 gram). To this solution silver nitrate (1.3 grams), dissolved in water, was added, when an almost colourless, gelatinous precipitate was produced:

0.2868 gave 0.0936 Ag. Ag=32.63.

$C_{10}H_8O_5NaAg$ requires Ag=32.73 per cent.

The Methyl Ether of Ethyl 5-Nitrocoumarate.—The methyl ether of silver 5-nitrocoumarate (1 gram), ethyl iodide (0.5 gram), and a little ether were heated together for three hours at 100°. After evaporating off the ether, the mixture was extracted with alcohol, from which solvent colourless needles, melting at 85°, were obtained:

0.1398 gave 0.2942 CO_2 and 0.0666 H_2O . C=57.38; H=5.29.

0.1716 „ 9.0 c.c. N_2 at 25° and 764 mm. N=5.88.

$C_{12}H_{13}O_5N$ requires C=57.37; H=5.18; N=5.58 per cent.

The Methyl Ether of Methyl 5-Nitrocoumarate.—The methyl ether of silver 5-nitrocoumarate (1 gram) was mixed with methyl iodide

(0.5 gram) and a little ether, and heated to 100° for three hours. After evaporating off the ether, the residue was extracted with alcohol, when colourless needles, melting at 163°, were obtained:

0.1050 gave 0.2150 CO₂ and 0.0454 H₂O. C=55.84; H=4.80.

0.1812 „ 9.9 c.c. N₂ at 764 mm. and 25°. N=6.07.

C₁₁H₁₁O₃N requires C=55.70; H=4.64; N=5.91 per cent.

5-Nitro-2-ethoxybenzaldehyde.—2-Ethoxybenzaldehyde was slowly added to nitric acid (D 1.5), the temperature being kept below 10°. After fifteen minutes the liquid was poured on crushed ice, and the precipitate crystallised from dilute alcohol. The substance crystallises in pale yellow needles, melting at 71–72°:

0.2910 gave 19.3 c.c. N₂ at 25° and 770 mm. N=7.54.

C₉H₉O₄N requires N=7.65 per cent.

The Ethyl Ether of 5-Nitrocoumaric Acid.—5-Nitro-2-ethoxybenzaldehyde (5 grams), anhydrous sodium acetate (5 grams), and acetic anhydride (15 grams) were boiled together for six hours. The cooled product was ground with water and extracted several times with ether. The ethereal extract was shaken with a solution of sodium carbonate, and the aqueous solution so obtained treated with an excess of hydrochloric acid, when a white precipitate was formed, which crystallised from dilute alcohol in colourless needles, melting at 194–195°:

0.1766 gave 0.3622 CO₂ and 0.0780 H₂O. C=55.94; H=4.91.

0.2288 „ 12.0 c.c. N₂ at 25° and 762 mm. N=5.87.

C₁₁H₁₁O₃N requires C=55.70; H=4.64; N=5.91 per cent.

The Ethyl Ether of Silver 5-Nitrocoumarate.—The ethyl ether of 5-nitrocoumaric acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1.7 grams), and a solution of silver nitrate (7.2 grams) then added, when the silver salt was precipitated as an almost colourless, gelatinous mass:

0.3620 gave 0.1132 Ag. Ag=31.27.

C₁₁H₁₀O₃NAg requires Ag=31.40 per cent.

The Ethyl Ether of Methyl 5-Nitrocoumarate.—The ethyl ether of silver 5-nitrocoumarate (1 gram), methyl iodide (0.5 gram), and a little ether were heated together at 100° for three hours. After evaporating the ether from the product, the residue was extracted with alcohol, from which solvent colourless needles, melting at 141–142°, were obtained:

0.1174 gave 0.2458 CO₂ and 0.0536 H₂O. C=57.10; H=5.07.

0.1624 „ 8.4 c.c. N₂ at 25° and 764 mm. N=5.80.

C₁₂H₁₂O₃N requires C=57.37; H=5.18; N=5.58 per cent.

The Bromine Additive Products.

Methyl $\alpha\beta$ -Dibromo-5-nitro-2-methoxy- β -phenylpropionate.—The methyl ether of methyl 5-nitrocoumarate (1 molecule) was dissolved in carbon disulphide, and treated with bromine (2.5 molecules). After twelve hours the liquid was evaporated, and the residue crystallised from alcohol. Colourless needles, melting at 126° , were obtained. The same product resulted when the methyl ether of methyl 5-nitrocoumarinate was treated in a similar manner:

0.1498 gave 0.1834 CO_2 and 0.0400 H_2O . $\text{C}=33.39$; $\text{H}=2.97$.

0.3806 „ 11.5 c.c. N_2 at 25° and 770 mm. $\text{N}=3.44$.

0.1460 „ 0.1380 AgBr. $\text{Br}=40.22$.

$\text{C}_{11}\text{H}_{11}\text{O}_5\text{NBr}_2$ requires $\text{C}=33.25$; $\text{H}=2.87$; $\text{N}=3.53$;

$\text{Br}=40.30$ per cent.

Methyl $\alpha\beta$ -Dibromo-5-nitro-2-ethoxy- β -phenylpropionate.—This compound was prepared from the ethyl ether of methyl 5-nitrocoumarate and bromine by the method described in the preceding experiment, and also by a similar treatment of the ethyl ether of methyl 5-nitrocoumarinate. The substance crystallises from alcohol in colourless needles, melting at 125° :

0.3010 gave 0.2760 AgBr. $\text{Br}=39.02$.

0.4020 „ 12.5 c.c. N_2 at 25° and 770 mm. $\text{N}=3.53$.

$\text{C}_{12}\text{H}_{12}\text{O}_5\text{NBr}_2$ requires $\text{N}=3.41$; $\text{Br}=38.93$.

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CCXXII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XVI.* The Relationship between the Chemical Constitution and the Influence of a Solvent.*

By THOMAS STEWART PATTERSON and ELIZABETH FINDLAY STEVENSON, M.A., B.Sc., Robert Donaldson Scholar of Glasgow University.

THE results which have been presented in former papers have made it clear that the rotation of ethyl tartrate, and doubtless also of many other active substances, responds in a remarkable manner to

* Part XV., Trans., 1909, 95, 1128.

differences in the constitution of the solvents in which the active compound may be dissolved. Thus, in $p=5$ solution in benzaldehyde, ethyl tartrate has a specific rotation of about $+45^\circ$ (Trans., 1909, 95, 322), whilst in benzantialdoxime at about the same concentration its specific rotation is approximately -12° , a difference of 57° . Not only can actual differences of composition produce such variations in rotation, but even the subtle difference of constitution in the *syn*- and *anti*-oximes can readily be detected in this way, whilst other methods of investigation, absorption spectroscopy, for example (Hartley and Dobbie, Trans., 1900, 77, 509), fail to indicate any dissimilarity.

It seems therefore possible that when a sufficient amount of orienting work has been done, an examination of the solvent effect of a given substance on the rotation of ethyl tartrate or other suitable active compound may throw valuable light on the constitution of the substance in question.

In our opinion the mechanism of this process is of a secondary character;* that is to say, the arrangement and relationship of the atoms of the solvent molecules produce a liquid which, in the mass, has at play within it certain characteristic forces, and an active compound dissolved in this liquid, coming under the influence of these forces, has its configuration and consequently its rotation altered as the result. The change of rotation is thus only an indirect effect of the chemical constitution of the solvent. In the first paper of this series the suggestion was made (Trans., 1901, 79, 188) that the proximate cause of solvent influence on rotation was that property of liquids known as internal pressure, and that variation of internal pressure from solvent to solvent might be indicated by variation of the solution-volume of the dissolved sub-

* As an instance of a primary effect we may cite absorption spectra. If it be the case, as seems generally to be held, that absorption bands are caused by vibrations inside the molecule which absorb light energy, then such an effect would be of a primary character, since it is directly transmitted to the medium in which it is observed. In regard to a primary effect, no two chemical compounds are likely to be absolutely identical, in much the same way that no two elements appear to have spectral lines in common, but substances of analogous composition will probably produce closely similar effects. On the other hand, however, two substances entirely dissimilar might quite well produce exactly the same secondary effect, just as a given strength of pull might be exerted either by a spring or by a system of gears, that is, in two very different ways. The boiling point of a liquid is a constitutive property of, at least, the second order, so that the same boiling point may be common to liquids having no chemical similarity. The melting point of a compound is a constitutive property of a higher order than the second. It is easy to see that the higher the order the more difficult it will be to interpret the effect, and this accounts for the striking failure to deduce any relationship between the simplest of physical properties, like boiling point, and especially melting point, and chemical constitution.

stance. It was also suggested that, since in solutions of finite concentration the total volume change is doubtless shared in by both constituents of the solution, it might be possible to correlate with rotation values, values of molecular solution-volume calculated for infinite dilution, the assumption being made, as a first approximation, that in very dilute solution the change of volume due to solution might be ascribed entirely to the solute. It is clear to us now, however, that this is an untenable assumption, although, of course, in some cases it may closely represent the truth, and thus account for certain regularities which were observed; in general, it could only be substantiated by a strict correspondence between experiment and theory, a correspondence which does not exist. A definite decision as to the existence of a relationship between rotation and solution-volume must be deferred until some method has been found of determining the true volume of the different constituents of a solution.

Some papers have recently appeared in which questions regarding internal pressure are discussed. Winther, in a number of valuable papers (*Zeitsch. physikal. Chem.*, 1907, **60**, 594, 651, 685), has attempted to carry the relationship between rotation and internal pressure much further than Patterson. Dawson (this vol., p. 1041) draws the conclusion that there is no connexion between internal pressure and solution-volume, but that, nevertheless, internal pressure and rotation may be correlative. His experiments point, he considers, to the existence in solutions of compound molecules of solvent and solute. On the other hand, Scheuer (*Zeitsch. physikal. Chem.*, 1910, **72**, 513), setting out with the view that the existence of such compounds is highly probable, was unable to find any evidence of their formation after a very complete and interesting examination of the melting-point curves, the volume relationships, the viscosity, the rotation, and the dispersion of mixtures of diethyl diacetyltartrate and of menthol with various inactive solvents. Amongst other less probable hypotheses, Scheuer therefore also suggests, like Patterson and Winther, that rotation changes on solution may be due to variation of internal pressure from solvent to solvent. It may be added that Grossmann (*Zeitsch. physikal. Chem.*, 1910, **73**, 148), using light of various wave-lengths, has examined the rotation of ethyl tartrate in a number of solvents, almost all of which had already been investigated by Patterson for yellow light. Grossmann is of opinion that his and other experiments render extremely probable the existence of compound molecules of solute and solvent, but no effort whatever is made to show how this conception would explain the results obtained.

Other attempts to establish the existence of compound molecules

of solvent and solute in solutions have been no more successful. Armstrong and his students have attacked the problem in various ingenious ways (*Proc. Roy. Soc.*, 1906, A, 78, 272; 1907, A, 79, 564, etc.), as has also Philip (*Trans.*, 1907, 91, 711), but further investigation by Usher (this vol., p. 66), and in a less degree by Findlay and Creighton (this vol., p. 536), has shown, at least, that the assumptions made in the particular method of attack are unwarranted.

In the absence of satisfactory proof of either view, it appears to us that the purely physical conception has the advantage of simplicity, and ought in the meantime to be adopted. In seeking, therefore, to correlate the chemical constitution of a given substance with its solvent influence, it should be carefully borne in mind that solvent influence being probably at least of a secondary character, any attempt to interpret it ought to be made with particular care.

In a recent paper of the present series (*Trans.*, 1908, 93, 1838), a commencement was made in the direction indicated, when it was shown by one of us that the solvent influence, on the rotation of ethyl tartrate, of disubstituted benzenes appeared to be governed by the general law that two substituting groups, similar or dissimilar, when in the ortho-position cause the greatest, and when in the para-position the least, rotation in the dissolved active ester. This behaviour was observed in regard to (1) *o*-, *m*-, and *p*-xylene; (2) *o*-, *m*-, and *p*-nitrotoluene; (3) *o*- and *m*-dinitrobenzene; (4) α - and β -nitronaphthalene; (5) 2:6- and 2:4-dinitrotoluene.

We have now examined, more or less completely, according to circumstances, the following solvents: phenol, anisole, phenetole, diphenyl ether; *o*-nitrophenol, *o*-nitroanisole, *o*-nitrophenetole; *m*-nitrophenol; *p*-nitrophenol, *p*-nitroanisole, *p*-nitrophenetole; catechol, resorcinol, quinol; pyrogallol, phloroglucinol; α -naphthol, β -naphthol; *p*-benzoquinone; and also *o*-, *m*-, and *p*-chloronitrobenzene.

A considerable number of these solvents are solids, in some cases of moderately high melting point, and it was therefore occasionally impossible either to examine dilute* solutions at all, or to examine even fairly concentrated solutions satisfactorily at a low temperature, which renders it difficult to institute wide comparisons between the data obtained for different solvents. So far as possible, however, we have extrapolated from our data to 20°, a standard temperature adopted in previous communications, even although many of the solutions could not possibly be examined in the polarimeter at that temperature, and in spite of the fact that the requisite extrapolation entails some loss of accuracy. In other cases

* With reference to ethyl tartrate.

comparison has been made at such temperatures as seemed most convenient.

Of the solvents mentioned above, but little need be said regarding the three last, and we may therefore commence with them. Only one solution in each, of approximately $p=25$, was made up and examined in the polarimeter at several different temperatures. As in this case it is only the relative effect of the *o*-, *m*-, and *p*-positions that comes in question, it is unnecessary to extrapolate to 20°; numbers are given below for the interpolated temperature 90°.

Ethyl Tartrate in o-, m-, and p-Chloronitrobenzene.

| Solvent. | M. p. | <i>p</i> . | α_D^{90} (100 mm.). | L_D^{90} .* |
|------------------------------------|-------|------------|----------------------------|---------------|
| <i>o</i> -Chloronitrobenzene | 32.5° | 25.733 | +7.26. | +28.2° |
| <i>m</i> -Chloronitrobenzene | 44.4 | 28.43 | 6.19 | 21.8 |
| <i>p</i> -Chloronitrobenzene | 83.0 | 24.26 | 3.8 | 15.7 |

* $R_D = 100 \alpha_D/p$; it does not differ much from specific rotation.

It is clear that in this set of compounds, also, as in the others already mentioned, the presence of the two substituents in the *o*-position brings about a much more powerful solvent influence than in either of the other two positions.

A general idea of the behaviour of most of the remaining solvents examined will be obtained from the diagram, which represents the effect of diluting ethyl tartrate with the various inactive compounds mentioned at a temperature of 20°, subject to the limitations referred to above.

Phenol (m. p. 42.5°).—Solution in phenol very greatly modifies the specific rotation of ethyl tartrate. The value rises from +7.8° in the pure ester to +43.5° at infinite dilution in phenol, an increase of 40.8°. Since benzene itself has but little effect (Trans, 1902, 81, 1098), it is clear that the introduction of the hydroxyl group must profoundly modify the interatomic forces of the molecule.

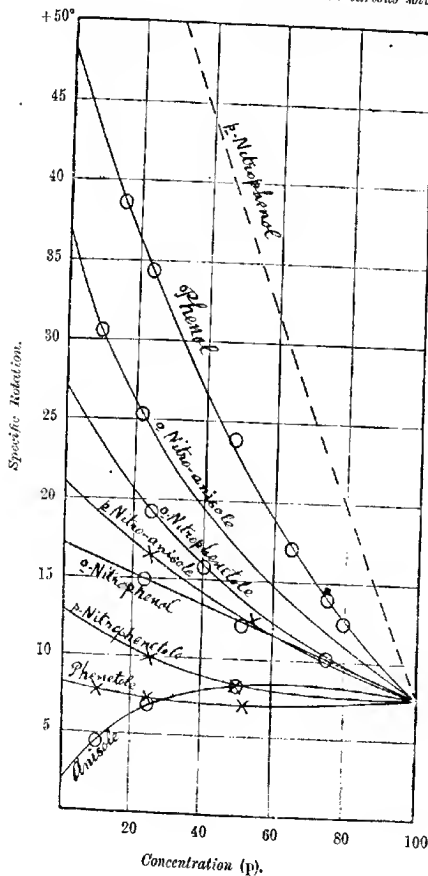
Anisole.—The replacement of the hydroxylic hydrogen by a methyl group brings with it a very great change in solvent influence. The specific rotation of the ethyl tartrate drops to +6.8° in a $p=25$ solution, that is, to a somewhat lower value than in the homogeneous ester. It will be noticed, too, that the shape of the concentration-rotation curve is of the opposite type to that of phenol, being concave to the point of origin of the diagram, in such a way that, starting from the value for the pure ester, the rotation increases slightly on dilution with anisole to reach a maximum value of about +8.2° between $p=50$ and 60, and then diminishes again fairly rapidly to about +2.5° at infinite dilution.

Phenetole.—In comparison with the difference between phenol and anisole, that between anisole and phenetole is slight. For

$p=25$ solutions the rotation values are much alike (anisole, $+6.8^\circ$; phenetole, $+7.32^\circ$), but it will be noticed that in regard to the form

FIG. 1.

Concentration-rotation curves for ethyl tartrate in various solvents.



of the concentration-rotation curve these two solvents differ, and at infinite dilution the values for the rotation of the dissolved ester are much more divergent ($+2.5^\circ$ and $+7.3^\circ$ respectively).

The curve for phenetole is of the same type as that for phenol; there is a minimum rotation of $+7^\circ$ at $p=50$, after which the rotation rises to reach the value $+8^\circ$ at infinite dilution.

Diphenyl Ether (m. p. 28°).—Only one solution was examined in diphenyl ether, of $p=24.58$. Its observed rotation at 20° was 1.95° , which, assuming a density of unity, gives a specific rotation of $+7.93^\circ$, about one degree higher than that in anisole and phenetole at the same temperature and concentration.

These results seem to make clear the fact that the powerful influence of phenol in this direction is to be attributed neither to the oxygen atom of the molecule nor to the phenyl group or—in the case of diphenyl ether—groups, but rather to the presence of the hydrogen atom of the hydroxyl group.

o-Nitrophenol (m. p. 45°).—Since an *o*-nitro-group in toluene and other monosubstituted benzenes produces a much greater increase of solvent influence than a *m*- or a *p*-nitro-group, we had expected that *o*-nitrophenol would have a greater influence than phenol. On the contrary, however, the rotation at infinite dilution ($+17^\circ$), although considerably higher than that of homogeneous ethyl tartrate, is much below the rotation in phenol. The effect of *o*-nitrophenol in this respect is in no way the mean of the effects of nitrobenzene and phenol, which are both above $+40^\circ$. The influence of the substituents is thus certainly not additive.

The concentration-rotation curve for *o*-nitrophenol is a straight line or nearly so.

o-Nitroanisole.—The exchange of the hydroxylic hydrogen atom of *o*-nitrophenol for a methyl group brings about, at infinite dilution, a considerable increase— 19.5° —in the rotation of the dissolved ester, namely, from $+17^\circ$ to $+36.5^\circ$.

o-Nitrophenetole.—In *o*-nitrophenetole the concentration-rotation curve is very similar to that for the corresponding methyl ether, but lies wholly below it. At infinite dilution the rotation would be $+27^\circ$.

There is thus between phenol and its ethers, on the one hand, and *o*-nitrophenol and its ethers on the other, a relationship of an inverse character when the solvent effects at infinite dilution are considered. In the former, the high rotation brought about by phenol gives place to a low rotation in anisole, and rises again somewhat in phenetole, whilst in the latter compounds the comparatively low value in *o*-nitrophenol rises to a fairly high value in *o*-nitroanisole, to fall again considerably in *o*-nitrophenetole.

p-Nitrophenol (m. p. 114°).—Owing to the higher melting points of the para-derivatives of phenol, observations could not be made, in this series, in so complete a fashion as in others, but sufficient

data have been obtained to elucidate the general behaviour of the compounds concerned. In *p*-nitrophenol, two solutions were examined in regard to rotation, density determinations, however, being omitted. In a solution of $p=47.86$ by interpolation from the observed data, $R_D^{100} = 34.6^\circ$,* whilst for $p=24.98$, $R_D^{100} = 46^\circ$, whence at infinite dilution, also for 100° , the value of R_D would be approximately $= 60^\circ$. These are very high values, and they increase as the temperature falls, so that at 20° the specific rotation, which in this case would have a slightly lower value than R_D , of an infinitely dilute solution of ethyl tartrate in *p*-nitrophenol would probably lie at about $+75^\circ$. *p*-Nitrophenol is thus considerably more powerful even than α -nitronaphthalene or *o*-dinitrobenzene, the most powerful of the solvents hitherto examined. But owing to the extensive extrapolation requisite in this case, the concentration-rotation curve for *p*-nitrophenol can only be regarded as a somewhat rough approximation, for which reason it is shown as a broken line in the diagram.

p-Nitroanisole (m. p. 54°).—This solvent on mixture with ethyl tartrate causes a gradual and comparatively slight increase of specific rotation. For a solution of $p=53.84$, $[\alpha]_D^{20} = +12.5^\circ$. By extrapolation of the observed readings for a $p=26.08$ solution, the value α_D^{20} (100 mm.) $= +5.1^\circ$ is found. Assuming a density of 1.2, which would certainly not be far from the truth, the specific rotation at infinite dilution would have a value of, approximately, $+21^\circ$.

p-Nitrophenetole (m. p. 60°).—Solutions of $p=49.66$ and $p=24.37$ were examined in this solvent. The specific rotations of these at 20° , assuming a density of 1.2 in each case, would be nearly $+8^\circ$ and $+10^\circ$. With increasing dilution, therefore, the rotation of the dissolved ethyl tartrate increases, although only slowly, to reach a value of about $+13^\circ$ at infinite dilution.

m-Nitrophenol (m. p. 96°).—Only one solution— $p=49.76$ —was examined. Its behaviour is referred to below.

2:4-Dinitrophenol (m. p. 114.5°).—We also examined one solution ($p=75.15$) in this substance. Its rotation was somewhat lower than that of an equally concentrated solution in *o*-nitrophenol.

General Discussion of the Foregoing Results.

1. We may examine first the solvent influence of phenol and its three nitro-derivatives, which will be best accomplished by considering the observed rotations for $p=50$ solutions at a temperature of 70° :

* See note on p. 2113.

| Solvent. | <i>p.</i> | α_D^{20} (100 mm.). | Difference. |
|-----------------------------|-----------|----------------------------|-------------|
| <i>o</i> -Nitrophenol | 51.13 | + 9.3° | 2.5° |
| Phenol | 48.2 | 11.8 | 3.5. |
| <i>m</i> -Nitrophenol | 49.76 | 15.3 | 2.4 |
| <i>p</i> -Nitrophenol | 47.88 | 17.7 | |

The influence of phenol is diminished 2.5° by the introduction of a nitro-group in the *o*-position; it is raised 3.5° by a nitro-group in the *m*-position and by a further 2.4° if the nitro-group be in the *p*-position, a behaviour which is thus just the opposite of that observed in other cases of ortho-, meta-, and para-isomerism.

2. Comparing the behaviour of phenol, *o*-nitrophenol, and *p*-nitrophenol with that of their respective ethers, it is to be noticed that the very great solvent influence of phenol disappears almost entirely in anisole, phenetole, and diphenyl ether, and that in a similar manner the very powerful effect of *p*-nitrophenol is greatly diminished in its methyl and ethyl ethers, and by an approximately equal amount in the two cases, some 50°. On the contrary, however, the comparatively feeble effect of *o*-nitrophenol is quite considerably raised in its ethers. Thus phenol and *p*-nitrophenol appear to behave in an analogous manner, and to differ from *o*-nitrophenol, as is shown in the table below.

Rotation of Ethyl Tartrate.

| Solvent. | $[\alpha]_D^{20}$ Infinite dilution. | Difference. | Solvent. | $[\alpha]_D^{20}$ Infinite dilution. | Difference. | Solvent. | $[\alpha]_D^{20}$ Infinite dilution. | Difference. |
|----------------|--|-------------|-----------------------------|--|-------------|-------------------------------|--|-------------|
| Phenol + 48.5° | | | <i>p</i> -Nitrophenol + 75° | | | <i>o</i> -Nitrophenol + 17° | | |
| Anisole. + 2.5 | + 46° | | <i>p</i> -Nitroanisole + 21 | + 54° | | <i>o</i> -Nitroanisole + 36.8 | - 10.8° | |

3. As shown in the following table, *o*-nitroanisole has a greater solvent influence than *p*-nitroanisole, and *o*-nitrophenetole a greater effect than *p*-nitrophenetole, and by almost the same amount.

Rotation of Ethyl Tartrate.

| Solvent. | $[\alpha]_D^{20}$ Infinite dilution. | Difference. | Solvent. | $[\alpha]_D^{20}$ Infinite dilution. | Difference. |
|----------------------------|--|-------------|------------------------------|--|-------------|
| <i>o</i> -Nitroanisole ... | + 36.8° | | <i>o</i> -Nitrophenetole ... | + 27° | 14° |
| <i>p</i> -Nitroanisole ... | 21.0 | 15.8° | <i>p</i> -Nitrophenetole ... | 13 | |

Although, therefore, the behaviour of the nitrophenols is unusual, inasmuch as the two substituting groups produce the greatest solvent effect when in the *p*-position, and least when in the *o*-position, this exceptional behaviour does not extend to their ethers, which exhibit the regularity previously described for the chloronitrobenzenes and a number of other substances.

4. It is of interest to compare, so far as is possible, our present results with some obtained by other methods having a similar aim. E. C. C. Baly and Miss Ewbank (Trans., 1905, **87**, 1315) have described the absorption curves for phenol, anisole, and phenetole. They point out that the curves for the others are identical, and that they differ in one particular* from that of phenol itself. This agrees roughly with what we have found, for, although the concentration-rotation curves for anisole, phenetole, and diphenyl ether are certainly not identical, still, in respect to the magnitude of their effect when compared with phenol, they are much alike. That for phenol differs very markedly.

We had also, during the course of this research, compared our results with the absorption curves given by Baly, Edwards, and Stewart (Trans., 1906, **89**, 512) for the nitrophenols and their ethers, but in a more recent paper Baly, Tuck and Marsden (this vol., p. 571) have explained the anomalous character of one earlier experimental result† as being due to solvent influence, and have considerably altered the theoretical views formerly held. They have rejected the idea of the existence of a quinonoid structure, not only in the free nitrophenols, but also in their alkali salts, and they draw the conclusion that *o*-nitrophenol and *o*-nitroanisole are similarly constituted, the same holding for the meta- and para-compounds.

It may be pointed out that our results, if it be legitimate to compare them with those of Baly, are not in agreement with this conclusion, since, as stated above, phenol and *p*-nitrophenol are related to their ethers in a similar manner, the solvent influence of the phenols being much greater than that of the ethers, whereas the opposite is the case for *o*-nitrophenol and its ethers. The ethers of phenol, *o*-nitrophenol, and *p*-nitrophenol, however, behave normally amongst themselves. It might therefore be concluded that phenol and *p*-nitrophenol are similar in structure and different from *o*-nitrophenol, but that the ethers are all of analogous constitution.

The data which we have obtained in the examination of a number of polyhydroxy-benzenes and of *p*-benzoquinone may be dealt with very briefly. In the table below, there are quoted interpolated values for the observed rotation at 100° of solutions all of about the same concentration.

* We are not aware what degree of importance Professor Baly would attribute to this difference.

† That the spectrum of *o*-nitroanisole differed from that of *o*-nitrophenol.

Rotation of Ethyl Tartrate.

| Solvent. | p . | α_D^{100} (100 mm.). |
|------------------------------|--------|-----------------------------|
| Benzene | 75.199 | +10.95* |
| Phenol | 74.39 | 13.82 |
| Catechol | 74.81 | 18.45 |
| Resorcinol | 74.10 | 16.55 |
| Quinol | 74.47 | 17.60 |
| Pyrogallol | 74.33 | 18.25 |
| Phloroglucinol | 74.33 | 17.20 |
| <i>p</i> -Benzoquinone | 74.98 | 10.90 |

* By extrapolation from figures given in Trans., 1902, 81, 116.

On account of the rather high melting points of these substances, only one concentrated solution in each was examined.

Catechol, Resorcinol, Quinol.—The first hydroxyl group introduced into the benzene ring produces a considerable increase of solvent influence. A second, however, in the *o*-position to the first, instead of causing a further increase, brings about a slight diminution of less than half a degree. In the *m*-position, on the other hand, an increase of nearly three degrees results, whilst in the *p*-position the increase is almost four degrees.

Pyrogallol, Phloroglucinol.—The behaviour of these two solvents is in remarkably close accordance with what might now be expected. The three hydroxyl groups in the vicinal position in pyrogallol bring about a small diminution as compared with catechol, whilst in the *m*-position in phloroglucinol there is a considerable increase as compared with resorcinol. It is thus quite clear that two hydroxyl groups have least effect in the *o*-position and most in the *p*-position, a behaviour which is thus similar to that shown by a nitro-group and a hydroxyl group when present together in the benzene ring, but opposite to that which is characteristic of two nitro-groups, two methyl groups, or a methyl group and a nitro-group.

p-Benzoquinone (m. p. 166°).—*p*-Benzoquinone, in a solution of approximately the same strength as for the polyhydroxy-benzenes, caused for α_D^{100} the value +10.9°, a considerably lower rotation than is produced by phenol or catechol. It might therefore be argued that a quinonoid structure of the solvent causes, in ethyl tartrate, a lower rotation than a simple phenolic constitution, and that therefore the low rotation produced by *o*-nitrophenol as compared with phenol and *p*-nitrophenol may be due to a quinonoid structure for the *o*-nitrophenol. We would not venture, of course, on this slight evidence, to draw any definite conclusion, but the fact is worthy of consideration along with others bearing on the question.

α - and β -Naphthol (m. p. 94° and 122°).—We also examined one

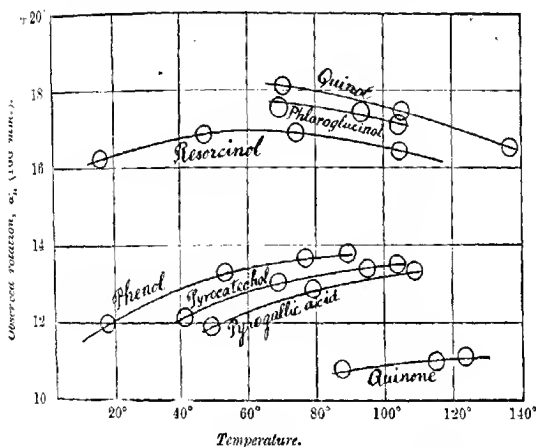
solution each in α - and β -naphthol. In the former, $R_D^{25.00}$ ($p=25.24$) = $+29.7^\circ$, and in the latter, $R_D^{29.01}$ ($p=29.01$) = $+43.8^\circ$. The difference is thus very considerable, and since the α -compound may be regarded as an o -hydroxy- and the β -compound as a m -hydroxy-derivative of benzene, the behaviour of these two solvents is strictly in accordance with that of the other phenols dealt with above.

Influence of Change of Temperature.

With regard to the influence of change of temperature on the rotation of these solutions, but little need be said, since the behaviour

FIG. 2.

Temperature-rotation curves for ethyl tartrate in various solvents
(p = approximately 75 in each case).



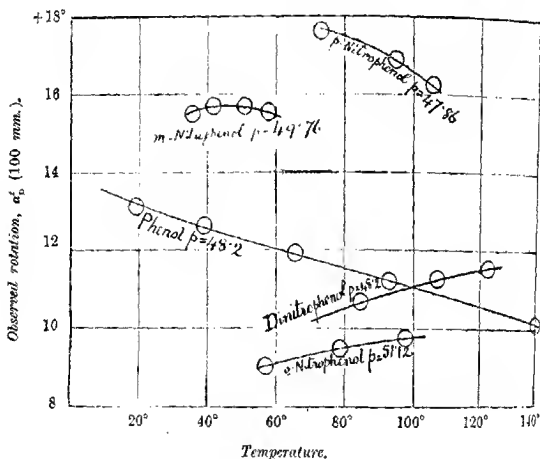
observed has been entirely in agreement with what has been discovered in other cases. The effect of rise or fall of temperature is a function of the value of the rotation at the temperature chosen. If the rotation at T° be above a certain critical value for that temperature, a value which can be fairly definitely stated,* then heating above T° will cause fall of rotation, whereas if the rotation be below the critical value, further heating will bring about increase of rotation. The temperature-rotation curves in Fig. 2 illustrate

* For 20° , for example, this critical value for specific rotation lies about $+18^\circ$ to $+20^\circ$.

this point. The rate at which the rotation increases with rise of temperature in pyrogallol ($p=74.93$) is greater than that in catechol solution of about the same concentration, in agreement with the fact that the rotation in the former solution is less than in the latter. In phenol, with its greater solvent influence, the rate of increase of rotation is less than in catechol. In resorcinol there is at first an increase of rotation and then a diminution, a maximum rotation occurring at a temperature of about 60° . This maximum rotation is therefore the critical value at 60° . Our data for phloroglucinol are rather scanty, but it is practically certain that

FIG. 3.

Temperature-rotation curves for ethyl tartrate in various solvents.



this solvent would show a similar behaviour, and therefore that a maximum rotation probably occurs at a lower temperature than 60° . In quinol only a fall of rotation was observed, but there is doubtless a maximum rotation somewhere about the temperature 40° , which would have a greater value than the maximum in phloroglucinol or in resorcinol. The critical value of the rotation is higher the lower the temperature at which it occurs.

The above remarks apply equally to the behaviour of α - and β -naphthol and the nitrophenols. In phenol itself it may be noted that whilst the temperature-rotation curves for solutions of high concentration are concave to the point of origin of the diagram,

that for a $p=50$ solution is almost a straight line but with a slight convexity, which, as the solutions are diluted, becomes gradually more pronounced. This resembles the behaviour of quinoline (Trans., 1909, 95, 323), and it is, of course, possible that others of the solvents we have dealt with would show the same behaviour in solutions more dilute than those we have investigated.

The experiments recorded in this paper seem, we think, to justify the conclusion that the chemical constitution of a solvent is not merely reflected—which, of course, it must be—but is reflected in a comparatively simple manner, in the influence of that solvent on the rotation of dissolved ethyl tartrate, and that, conversely, this method might be used for the investigation of chemical constitution. The method differs from that of refractive index and of magnetic rotation, inasmuch as it does not seem possible to calculate any constant increment or decrement for a given group of atoms, for a single atom or for a difference in the linking of an atom in the molecule, but these are certainly indicated qualitatively. There is perhaps a closer connexion between the phenomena we have described and those of absorption spectroscopy. So far as we are able to judge, knowing only one of these methods intimately, the solvent-influence of a compound on the rotation of ethyl tartrate affords a more delicate criterion of chemical constitution than either of the others, as witness, for example, the effect of ortho-, meta-, and para-isomerism, the difference between phenol and anisole, and especially the difference between the *syn*- and *anti*-oximes. We hope to describe the further study of the subject in future papers.

EXPERIMENTAL.

*Ethyl Tartrate in Various Solvents.**o*-Chloronitrobenzene. $p=25.73$:

| | | | | | | |
|-------------------------------|-------|--------|--------|-------|-----|-------|
| t | 21.7° | 30.55° | 40.55° | 49.2° | 56° | 62.9° |
| α_D^{20} (100 mm.) ... | 7.7 | 7.654 | 7.638 | 7.61 | 7.5 | 7.33 |

m-Chloronitrobenzene. $p=28.43$:

| | | | | | |
|-------------------------------|-------|-------|-------|-------|--------|
| t | 36.9° | 52.2° | 77.4° | 89.7° | 105.2° |
| α_D^{20} (100 mm.) ... | 5.754 | 5.9 | 6.125 | 6.046 | 6.236 |

p-Chloronitrobenzene. $p=24.26$:

| | | | | | |
|-------------------------------|-------|--------|-------|--------|--------|
| t | 82.1° | 105.2° | 117° | 128.2° | 147.1° |
| α_D^{20} (100 mm.) ... | 3.735 | 3.885 | 4.098 | 4.106 | 4.12 |

6 z 2

*Ethyl Tartrate in Various Solvents (continued).**Phenol.*I. $p=14.79$:

| | | | | | |
|----------------------------|-------|--------|--------|--------|-------|
| t | 20° | 30.75° | 52.3° | 69.5° | 92.4° |
| α_p^t (100 mm.) ... | — | +5.695 | +4.885 | +4.525 | 4.085 |
| $[\alpha]_p^t$ | +38.5 | +35.47 | +30.96 | +29.10 | 26.85 |

II. $p=23.85$:

| | | | | | | | | |
|----------------------------|--------|-------|-------|-------|-------|-------|-------|--------|
| t | 18.8° | 20° | 32.4° | 41.9° | 53.5° | 65.5° | 98.9° | 130.4° |
| α_p^t (100 mm.) ... | +9.039 | — | 8.445 | 8.031 | 7.586 | 7.23 | 6.345 | 5.665 |
| $[\alpha]_p^t$ | 34.25 | +34.2 | 32.32 | 30.98 | 29.55 | 28.42 | 25.7 | 23.65 |

III. $p=48.2$:

| | | | | | | |
|----------------------------|---------|-------|-------|-------|-------|--------|
| t | 19° | 20° | 39° | 65.2° | 92.3° | 140.6° |
| α_p^t (100 mm.) ... | +13.124 | — | 12.64 | 11.95 | 11.27 | 10.16 |
| $[\alpha]_p^t$ | 23.99 | 23.94 | 23.44 | 22.62 | 21.83 | 20.54 |

IV. $p=64.78$:

| | | | | | |
|----------------------------|-------|--------|--------|--------|-------|
| t | 20° | 20.9° | 64.9° | 100.3° | 126° |
| α_p^t (100 mm.) ... | — | 12.853 | 13.309 | 13.058 | 12.7 |
| $[\alpha]_p^t$ | 17.05 | 17.10 | 18.33 | 18.73 | 18.52 |

V. $p=74.39$:

| | | | | | |
|----------------------------|--------|-------|--------|-------|--------|
| t | 18.75° | 20° | 53.5° | 76.5° | 89.7° |
| α_p^t (100 mm.) ... | 11.99 | — | 13.225 | 13.02 | 13.775 |
| $[\alpha]_p^t$ | 13.73 | 13.32 | 15.60 | 16.38 | 16.76 |

VI. $p=79.24$:

| | | | | | |
|----------------------------|--------|--------|--------|--------|--------|
| t | 19.95° | 20° | 55.5° | 87.1° | 117.2° |
| α_p^t (100 mm.) ... | 11.485 | 11.534 | 13.248 | 14.018 | 14.209 |
| $[\alpha]_p^t$ | 12.30 | 12.37 | 14.62 | 15.90 | 16.62 |

Densities Determined.

| I. | | II. | | III. | |
|-------|--------|-------|--------|-------|--------|
| t . | d . | t . | d . | t . | d . |
| 38.5° | 1.0787 | 21.4° | 1.1050 | 11.9° | 1.1404 |
| 45.4 | 1.0725 | 37.9 | 1.0903 | 33.5 | 1.1232 |
| 66.4 | 1.0539 | 58.2 | 1.0721 | 46.5 | 1.1133 |
| 78.8 | 1.0431 | 78.1 | 1.0538 | 74.6 | 1.0878 |
| | | 99.8 | 1.0332 | 99.2 | 1.0640 |
| IV. | | V. | | VI. | |
| t . | d . | t . | d . | t . | d . |
| 14.6° | 1.1665 | 16.1° | 1.1755 | 13.5° | 1.1887 |
| 35.5 | 1.1451 | 28.7 | 1.1635 | 38.4 | 1.1606 |
| 55.8 | 1.1261 | 42.0 | 1.1499 | 58.4 | 1.1412 |
| 83.4 | 1.0997 | 64.7 | 1.1284 | 82.1 | 1.1176 |

*Ethyl Tartrate in Various Solvents (continued).**Anisole.*I. $p=9.99$:

| | | | | |
|--------------------------------|---------|-------|---------|---------|
| t | 18.2° | 20° | 27.3° | 35.2° |
| α_D^{20} (100 m.) | + 0.432 | — | + 0.536 | + 0.622 |
| $[\alpha]_D^{20}$ | + 4.27 | + 4.5 | + 5.34 | + 6.25 |

II. $p=24.62$:

| | | | | | | | |
|---------------------------------|---------|-----|-------|-------|-------|-------|-------|
| t | 14.6° | 20° | 33.2° | 46.8° | 52.9° | 68.9° | 72.8° |
| α_D^{20} (100 mm.) | + 1.602 | — | 2.068 | 2.428 | 2.512 | 2.952 | 3.012 |
| $[\alpha]_D^{20}$ | + 6.24 | 6.8 | 8.20 | 9.75 | 10.15 | 12.11 | 12.41 |

III. $p=49.85$:

| | | | |
|---------------------------------|-------|-----|-------|
| t | 19° | 20° | 30.6° |
| α_D^{20} (100 mm.) | 4.324 | — | 4.904 |
| $[\alpha]_D^{20}$ | 7.96 | 8.1 | 9.12 |

Densities Determined.

| I. | | II. | | III. | |
|-------|--------|-------|--------|-------|--------|
| t . | d . | t . | d . | t . | d . |
| 17.5° | 1.0142 | 14.9° | 1.0424 | 15.8° | 1.0933 |
| 25.4 | 1.0064 | 32.5 | 1.0261 | 25.6 | 1.0835 |
| — | — | 45.5 | 1.0130 | — | — |
| — | — | 55.5 | 1.0033 | — | — |

*Phenol.*I. $p=9.99$:

| | | | | | |
|---------------------------------|--------|------|-------|-------|-------|
| t | 19.5° | 20° | 22.1° | 27.1 | 36.5° |
| α_D^{20} (100 mm.) | + 0.76 | — | 0.786 | 0.822 | 0.928 |
| $[\alpha]_D^{20}$ | + 7.72 | 7.75 | 8.00 | 8.41 | 9.58 |

II. $p=24.96$:

| | | | | | |
|---------------------------------|---------|------|-------|-------|-------|
| t | 19.2° | 20° | 31.6 | 43.5 | 50.5 |
| α_D^{20} (100 mm.) | + 1.832 | — | 2.202 | 2.51 | 2.686 |
| $[\alpha]_D^{20}$ | + 7.23 | 7.32 | 8.79 | 10.14 | 10.92 |

III. $p=51.73$:

| | | | |
|---------------------------------|---------|--------|-------|
| t | 18.2° | 20° | 31.0° |
| α_D^{20} (100 mm.) | + 3.742 | — | 4.432 |
| $[\alpha]_D^{20}$ | + 6.72 | + 6.86 | 8.05 |

Densities Determined.

| I. | | II. | | III. | |
|-------|--------|-------|--------|-------|--------|
| t . | d . | t . | d . | t . | d . |
| 18.6° | 0.9862 | 17.9° | 1.0161 | 17.7° | 1.0772 |
| 25.8 | 0.9794 | 28.1 | 1.0071 | 26.5 | 1.0683 |
| — | — | 38.3 | 0.9969 | — | — |
| — | — | 48.4 | 0.9869 | — | — |

*Ethyl Tartrate in Various Solvents (continued).**Diphenyl Ether.* $p = 24.58:$

| | | | | | |
|---------------------------------|---------|------|-------|-------|-------|
| t | 18.7° | 20° | 51.8° | 66.0° | 76.3° |
| α_D^{20} (100 mm.) | + 1.824 | 1.95 | 2.68 | 2.92 | 8.288 |

*o-Nitrophenol.*I. $p = 23.89:$

| | | | |
|---------------------------------|---------|-------|--------|
| t | 60.1° | 81.4° | 112.2° |
| α_D^{20} (100 mm.) | + 4.82 | 4.972 | 5.007 |
| $[\alpha]_D^{20}$ | + 16.20 | 16.98 | 17.66 |

II. $p = 51.12:$

| | | | |
|---------------------------------|---------|-------|-------|
| t | 56.8° | 78.2° | 97.3° |
| α_D^{20} (100 mm.) | + 9.015 | 9.488 | 9.766 |
| $[\alpha]_D^{20}$ | + 14.31 | 15.35 | 16.08 |

III. $p = 74.95:$

| | | | | |
|---------------------------------|---------|--------|-------|--------|
| t | 16° | 43.4° | 87.3° | 115.1° |
| α_D^{20} (100 mm.) | + 9.142 | 11.119 | 12.66 | 13.058 |
| $[\alpha]_D^{20}$ | + 9.74 | 12.14 | 14.38 | 14.21 |

Densities Determined.

| I. | | II.* | | III. | |
|-------|--------|-------|--------|-------|--------|
| t | d | t | d | t | d |
| 47.7° | 1.2803 | 56.8° | 1.2323 | 12.5° | 1.2558 |
| 65.9 | 1.2416 | 78.2 | 1.2086 | 27.1 | 1.2385 |
| 78.1 | 1.2295 | 97.3 | 1.1878 | 49.4 | 1.2164 |
| — | — | — | — | 72.5 | 1.1910 |

* By interpolation from the determinations for the other two solutions.

*o-Nitroanisole.*I. $p = 9.79:$

| | | | | | | |
|-------------------------------|---------|------|-------|-------|-------|-------|
| t | 17.9° | 20° | 34.5° | 43.8° | 53.2° | 62.8° |
| α_D^{20} (100 mm.) ... | + 3.748 | — | 3.548 | 3.490 | 3.354 | 3.26 |
| $[\alpha]_D^{20}$ | + 30.7 | 30.6 | 29.5 | 29.2 | 28.3 | 27.7 |

II. $p = 21.17:$

| | | | | | | |
|-------------------------------|-------|------|-------|-------|-------|-------|
| t | 17.4° | 20° | 29.1° | 39.3° | 50° | 55.8° |
| α_D^{20} (100 mm.) ... | 6.666 | — | 6.604 | 6.472 | 6.442 | 3.24 |
| $[\alpha]_D^{20}$ | 25.35 | 25.3 | 25.4 | 25.1 | 25.2 | 24.8 |

Densities Determined.

| I. | | II. | |
|-------|--------|-------|--------|
| t | d | t | d |
| 17.7° | 1.2471 | 14.9° | 1.2442 |
| 33 | 1.2319 | 35 | 1.2237 |
| 42.9 | 1.2219 | 53.2 | 1.2053 |
| 59.7 | 1.2050 | 66.4 | 1.1919 |

*Ethyl Tartrate in Various Solvents (continued).**o-Nitrophenetole.*I. $p=25.09$:

| | | | | | |
|-------------------------------|---------|-------|-------|-------|-------|
| t | 18.4° | 20° | 30.8° | 53.3° | 65.5° |
| α_D^{20} (100 mm.) ... | + 5.693 | — | 5.812 | 5.906 | 5.898 |
| $[\alpha]_D^{20}$ | +19.11 | -19.2 | 19.7 | 20.41 | 20.6 |

II. $p=39.43$:

| | | | | | |
|-------------------------------|---------|-------|-------|-------|-------|
| t | 15.9° | 20° | 25.1° | 29.1° | 42° |
| α_D^{20} (100 mm.) ... | + 7.252 | — | 7.544 | 7.57 | 7.848 |
| $[\alpha]_D^{20}$ | +15.41 | 15.75 | 16.16 | 16.27 | 17.06 |

Densities Determined.

| I. | | II. | |
|-------|--------|-------|--------|
| t . | d . | t . | d . |
| 17.1° | 1.1896 | 14.6° | 1.1948 |
| 33.4 | 1.1734 | 25.9 | 1.1833 |
| 40.4 | 1.1659 | 33.3 | 1.1757 |
| 54.3 | 1.1524 | 41 | 1.1680 |

p-Nitrophenol. $p=24.93$:

| | | |
|-----------------------------|---------|--------|
| t | 105.9° | 120° |
| α_D^{20} (100 mm.) + | 11.262 | 10.646 |
| $[\alpha]_D^{20}$ | + 45.09 | 42.62 |

 $p=47.86$:

| | | |
|---------|--------|--------|
| 72.6° | 94.5° | 103.7° |
| +17.624 | 16.878 | 16.274 |
| +36.82 | 35.27 | 34.0 |

p-Nitroanisole. $p=26.08$:

| | | | | | |
|---------------------------------|---------|-------|-------|-------|-------|
| t | 52.0° | 55.3° | 64.8° | 73.6° | 77° |
| α_D^{20} (100 mm.) | + 6.082 | 6.26 | 6.515 | 6.075 | 6.078 |

 $p=53.84$:

| | | | | | |
|-------------------------------|-------|---------|-------|-------|-------|
| t | 20° | 35.1° | 44.4° | 51.3° | 57.6° |
| α_D^{20} (100 mm.) ... | — | + 8.876 | 9.198 | 9.376 | 9.54 |
| $[\alpha]_D^{20}$ | +12.5 | +13.63 | 14.23 | 14.58 | 14.91 |

Densities Determined.

| | | | | |
|-------|--------|--------|--------|--------|
| t . | 35.1° | 41.4° | 48° | 57.2° |
| d . | 1.2101 | 1.2038 | 1.1974 | 1.1883 |

p-Nitrophenetole. $p=24.37$:

| | | | | | | | | |
|-------------------------------|--------|-------|-------|-------|---------|-------|-------|-------|
| t | 50.1° | 57.3° | 67.3° | 82.5° | 49.4° | 54.4° | 66.6° | 69.7° |
| α_D^{20} (100 mm.) ... | + 3.88 | 3.995 | 4.21 | 4.345 | + 6.475 | 6.73 | 7.175 | 7.25 |

 $p=49.66$:*m-Nitrophenol.* $p=49.76$:

| | | | | |
|-------------------------------|-------|-------|--------|-------|
| t | 35.4° | 41.4° | 50.3° | 57.7° |
| α_D^{20} (100 mm.) ... | +15.5 | 15.68 | 15.665 | 15.55 |

Ethyl Tartrate in Various Solvents (continued).

2: 4-Dinitrophenol (m. p. 114·5°).

 $p = 75\cdot15$:

| | | | |
|---------------------------------|---------|--------|--------|
| t | 84·5° | 107° | 121·5° |
| α_D^{25} (100 mm.) | +10·696 | 11·272 | 11·564 |

Catechol. $p = 74\cdot81$:

| | | | | |
|---------------------------------|--------|-------|-------|--------|
| t | 41·4° | 68·9° | 94·3° | 103·7° |
| α_D^{25} (100 mm.) | +12·12 | 13·04 | 13·40 | 13·53 |

Resorcinol. $p = 74\cdot12$:

| | | | | |
|---------------------------------|--------|-------|-------|--------|
| t | 15·9° | 47·7° | 74·3° | 104·2° |
| α_D^{25} (100 mm.) | +16·25 | 16·86 | 16·89 | 16·644 |

Quinol. $p = 74\cdot47$:

| | | | |
|---------------------------------|-------|------|--------|
| t | 70·3° | 105° | 136·5° |
| α_D^{25} (100 mm.) | +18·1 | 17·5 | 16·53 |

Pyrogallol. $p = 74\cdot93$:

| | | | |
|---------------------------------|--------|--------|--------|
| t | 49·5° | 78·9° | 106·6° |
| α_D^{25} (100 mm.) | 11·884 | 12·883 | 13·344 |

Phloroglucinol. $p = 74\cdot33$:

| | | | |
|---------------------------------|--------|-------|--------|
| t | 69·5° | 93·6° | 104·1° |
| α_D^{25} (100 mm.) | +17·48 | 17·43 | 17·10 |

 α -Naphthol. $p = 25\cdot24$:

| | | |
|---------------------------------|--------|--------|
| t | 195·6° | 121·5° |
| α_D^{25} (100 mm.) | +7·276 | 6·732 |

 β -Naphthol. $p = 29\cdot01$:

| | | |
|---------------------------------|--------|--------|
| t | 132·7° | 150° |
| α_D^{25} (100 mm.) | +10·92 | +9·988 |

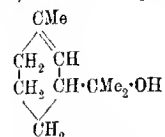
p-Benzoquinone. $p = 74\cdot98$:

| | | | |
|---------------------------------|---------|--------|--------|
| t | 87·5° | 115° | 122·9° |
| α_D^{25} (100 mm.) | +10·804 | 10·963 | 11·123 |

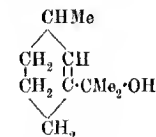
CCXXIII.—*Experiments on the Synthesis of the Terpenes.*
Part XIV. Synthesis of d- and l-Δ⁵-m-Menthenol(8),
dl-Δ⁴-m-Menthenol(8) and their Derivatives.

By WILLIAM HENRY PERKIN, jun.

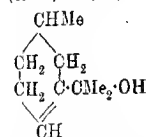
Of the six possible menthenols of the meta-series,* the following four have, so far, been synthesised:



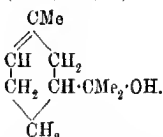
Δ¹ (Dihydrocarvestrenol)
 (Trans., 1907, 91, 493.)



(Δ²)
 (Trans., 1905, 87, 1101.)

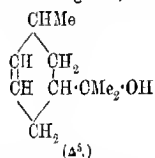


(Δ³) (Trans., 1905, 87, 1099;
 compare this vol., p. 1029.)

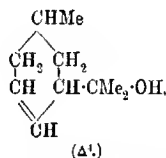


Δ⁶ (Dihydroisocarvestrenol).
 (Trans., 1903, 93, 1837.)

The present communication contains an account of the synthesis of the remaining two, namely:

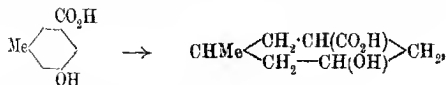


and



Of the former, the *d*- and *l*- and *dl*-modifications have been prepared, whereas of the latter only the *dl*-modification was obtained, and that in very small quantity.

A short time since (Trans., 1909, 95, 1889), Meldrum and Perkin showed that 5-hydroxy-*m*-toluic acid is reduced by sodium and amyl alcohol to 1-methylcyclohexan-5-ol-3-carboxylic acid †:

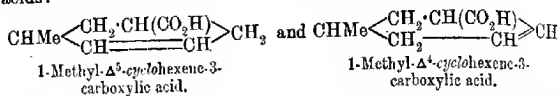


* Menthenols of the type of terpineol are here referred to.

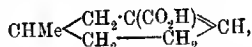
† In the paper referred to, this acid was called "1-methylcyclohexan-3-ol-5-carboxylic acid," but the alternative numbering is more suitable.

and, in the present communication, it is shown that this reduction may also be effected in alcoholic solution, provided that the alcohol has been completely dehydrated by distillation over calcium.

When 1-methylcyclohexan-5-ol-3-carboxylic acid is treated with hydrobromic acid, it is readily converted into 5-bromo-1-methylcyclohexane-3-carboxylic acid, and the ester of this acid, when digested with diethylamine, yields a mixture of the esters of the acids:

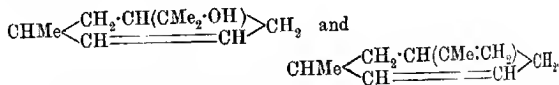


and these acids, of which the former is produced in by far the larger quantity,* were separated by the fractional crystallisation of their calcium salts. The constitution of the former of these acids (Δ^5) was demonstrated by the examination of the products of the oxidation of Δ^5 -*m*-menthenol(8) obtained from its ester by the action of magnesium methyl iodide (p. 2132). The constitution of the other acid (Δ^4) was proved by the fact that, when boiled with concentrated aqueous potassium hydroxide, it is converted into 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid:



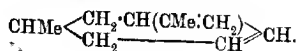
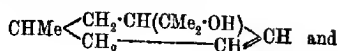
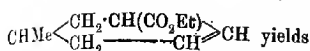
the $\beta\gamma$ -unsaturated acid becoming $\alpha\beta$ - in the usual manner.

Ethyl *dl*-1-methyl- Δ^4 -cyclohexene-3-carboxylate reacts readily with magnesium methyl iodide with the formation of *dl*- Δ^5 -*m*-menthenol(8) (b. p. 115–117°/30 mm.), and this, when boiled with aqueous oxalic acid, yields *dl*- Δ^6 :8(9)-*m*-menthadiene (b. p. 175–176°):



Under similar conditions, ethyl *dl*-1-methyl- Δ^4 -cyclohexene-3-carboxylate yields Δ^4 -*m*-menthenol(8) (b. p. 115–117°/30 mm.) and Δ^4 :8(9)-*m*-menthadiene (b. p. 175–177°):

* It has often been observed, in cases where two isomeric unsaturated acids are formed by the elimination of hydrogen bromide from a bromo-acid, that very slight changes in the conditions of experiment often effect in a remarkable manner the proportions of the isomerides produced. Two experiments were made on the elimination of hydrogen bromide from ethyl 5-bromo-1-methylcyclohexane-3-carboxylate by means of diethylamine. In the one the yield of 1-methyl- Δ^4 -cyclohexene-3-carboxylic acid obtained on hydrolysis was 5 per cent., in the other, apparently under the same conditions, the yield was less than 1 per cent.



Resolution of dl-1-Methyl- Δ^5 -cyclohexene-3-carboxylic Acid and Preparation of the d- and l-Modifications of Δ^5 -m-Menthenol(8).

As the amount of pure *dl*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid which had accumulated during these experiments amounted to more than 160 grams, it was thought that it would be interesting to attempt its resolution, and then to convert the active acids into the corresponding menthenols and menthadienes. This was ultimately accomplished with the aid of either *l*-menthylamine or quinine, the salt produced in both cases being the salt of the dextro-acid.

The *l*-menthylamine salt, after repeated recrystallisation, had $[\alpha]_D -1.7^\circ$, and from this salt the acid was regenerated and converted into its ester and the corresponding menthenol and terpene by processes already described in the case of the *dl*-acid. The observed rotations of these substances may be conveniently tabulated thus:

| | |
|---|--------------------|
| <i>d</i> -1-Methyl- Δ^5 -cyclohexene-3-carboxylic acid | $[\alpha]_D$ |
| Ethyl <i>d</i> -1-methylcyclohexenecarboxylate | + 33.1° |
| <i>d</i> - Δ^5 - <i>m</i> -Menthenol(8) | + 30.5 |
| <i>d</i> - Δ^5 - <i>m</i> -Menthadiene | + 36.7 |
| | + 29.6 |

After the *d*-acid had been removed, as far as practicable, by treatment with *l*-menthylamine and quinine, the *l*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid, contained in the mother liquor of these salts, was nearly pure, since its rotation was $[\alpha]_D -30.9^\circ$, as compared with the rotation $[\alpha]_D +33.1^\circ$ of the corresponding *d*-acid.

From this *l*-acid the same derivatives were prepared as in the case of the *d*-acid, and these and their rotations may again be tabulated:

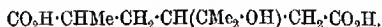
| | |
|---|--------------------|
| <i>l</i> -1-Methyl- Δ^5 -cyclohexene-3-carboxylic acid | $[\alpha]_D$ |
| Ethyl <i>l</i> -1-methylcyclohexenecarboxylate | - 30.9° |
| <i>l</i> - Δ^5 - <i>m</i> -Menthenol(8) | - 27.4 |
| <i>l</i> - Δ^5 - <i>m</i> -Menthadiene | - 32.6 |
| | - 25.3 |

The constitutions assigned to these active menthenols and menthadienes, and indirectly therefore those of the corresponding

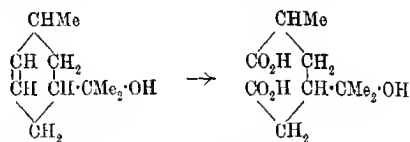
inactive substances and also that of 1-methyl- Δ^5 -cyclohexene-3-carboxylic acid, were proved in the following manner.

Pure *d*- Δ^5 -*m*-menthenol(8) was oxidised with permanganate and then with dichromate under the conditions described on p. 2143, and the resulting acid converted into the ethyl ester, which was purified by fractional distillation under diminished pressure. The ester, $C_{12}H_{20}O_4$, thus obtained distilled at $188-190^\circ/20$ mm., and had $[\alpha]_D -18.7^\circ$.

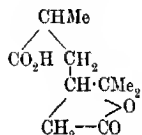
When this ester was hydrolysed, it yielded a mixture of two isomeric lactonic acids, $C_{10}H_{16}O_4$, which melt at 102° and 136° respectively, and are obviously the *cis*- and *trans*-lactones of α -methyl- γ -hydroxyisopropyladipic acid:



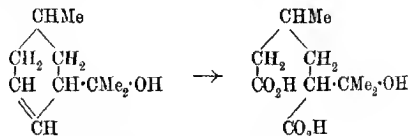
The formation of this acid by the oxidation of Δ^5 -*m*-menthenol(8) may be expressed in the following manner:



and its easy conversion into the lactone:



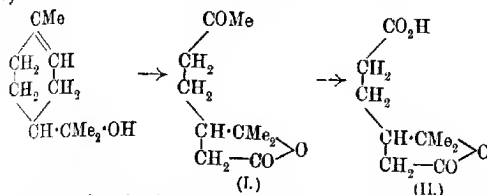
proves that the menthenol from which it is derived must have the double linking in the Δ^5 -position, since the dibasic acid which might result from the oxidation of the menthenol of the other alternative constitution (Δ^4):



would hardly be expected to pass into a lactone.

The oxidation of *d*- Δ^5 -*m*-menthenol(8) is very similar to that of ordinary terpineol, which, with chromic acid, yields methoethylheptanonolide (I), and then, with hypobromite, homoterpenylic acid

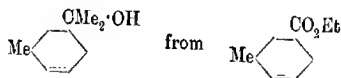
(II) (Wallach, *Ber.*, 1895, **28**, 1773; Tiemann and Semmler, *ibid.*, 2141):



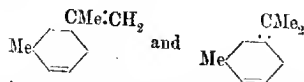
A similar series of oxidations carried out with *l*- Δ^5 -*m*-menthenol(8) gave again the ester, $\text{C}_{12}\text{H}_{20}\text{O}_4$, of the mixed lactic acids. This had $[\alpha]_D + 17.4^\circ$, and yielded, on hydrolysis, the *cis*- and *trans*-lactones of melting points 102° and 136° , which had been obtained from the *d*-modification. Moreover, it is curious that, whilst the ester, $\text{C}_{12}\text{H}_{20}\text{O}_4$, was, in both cases, optically active, the lactones obtained on hydrolysis, although they still contain two asymmetric carbon atoms, should prove to be inactive.

These oxidation experiments show conclusively not only that the two active series tabulated on p. 2131 represent *d*- and *l*-modifications of the same substances, but also that these substances have the constitutions which have been assigned to them.

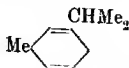
In connexion with this series of researches on the synthesis of the terpenes, there is one point of importance which should be made quite clear. When a menthenol is synthesised from the ester of the corresponding acid by the action of magnesium methyl iodide, for example:



the menthenol which is obtained is quite pure and homogeneous. When, however, water is eliminated from such a menthenol, the resulting menthadiene is probably, as a rule, not a homogeneous substance, but may consist of a mixture, in varying proportions, of the isomerides:

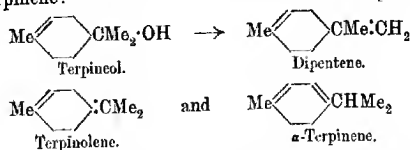


and possibly, owing to intramolecular change, the third isomeride of the type:



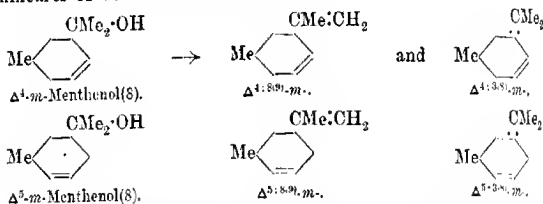
may also be present. It is well known, especially from the

researches of Wallach, that ordinary terpineol, on treatment with dehydrating agents, yields not only dipentene, but also terpinolene and α -terpinene:



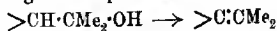
The conversion of terpineol into terpinolene appears to take place most readily when dilute acids are used as the dehydrating agent. Thus, Baeyer (*Ber.*, 1894, **27**, 447) recommends 30 per cent. oxalic acid as the best reagent for converting terpineol into terpinolene.

In the present communication it is stated that the reagent which was found most suitable for the elimination of water from Δ^4 and Δ^5 -*m*-menthenol(8) was 6 per cent. oxalic acid, and it seems therefore very probable that the products obtained in each case may be mixtures of at least two menthadienes:



It would be difficult to separate and identify such isomeric products of the elimination of water even if large quantities of the menthenols were available, and, in the present case, where the preparation of even small quantities of material is very laborious, this problem cannot, in the meantime, be solved. It has therefore been decided to retain for the present the names $\Delta^4\text{:8(9)}$ and $\Delta^5\text{:8(9)}$ -*m*-menthadiene for the hydrocarbons, and the determination of the exact nature of these products of dehydration must be left until a better method for their preparation has been discovered. When larger quantities of material are available, an effort will also be made accurately to determine the physical constants of all the substances mentioned in this paper.

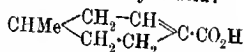
The probability that substances of the terpinolene type are frequently produced during the elimination of water from the menthenols according to the process:



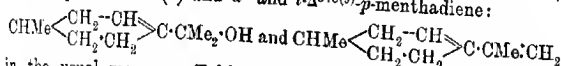
suggests an explanation for some of the remarkable results which

have been obtained, more particularly during the course of the investigation of optically active menthenols and menthadienes. In the first place, it is important to note that the above process cannot take place when the $>\text{CMe}_2\cdot\text{OH}$ group is attached to a doubly linked carbon atom, as in $>\text{C}\cdot\text{CMe}_2\cdot\text{OH}$. Apart from fundamental intramolecular change, which both chemical properties and physical measurements show to be most improbable, menthenols containing this grouping can only yield conjugated menthadienes containing the grouping $>\text{C}\cdot\text{CMe}\cdot\text{CH}_2$, and there can be little doubt that the several synthetical menthadienes of this type which have already been described (compare this vol., p. 2154) are pure individuals.

Some time since, Kay and Perkin (Trans., 1906, 89, 840) resolved *dl*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid:



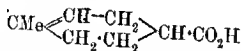
into its active constituents, and prepared from the *d*- and *l*-acids, *d*- and *l*-*p*-menthenol(8) and *d*- and *l*- Δ^3 : Δ^9 -*p*-menthadiene:



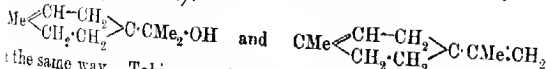
in the usual manner. Taking the *d*-series as the example, the optical activity of these substances may be conveniently tabulated:

| | |
|---|--------------|
| <i>d</i> -1-Methyl- Δ^3 -cyclohexene-4-carboxylic acid | $[\alpha]_D$ |
| Ethyl <i>d</i> -1-methylcyclohexenecarboxylate | +101.1° |
| <i>d</i> - Δ^3 - <i>p</i> -Menthenol(8) | +96.5 |
| <i>d</i> - Δ^3 : Δ^9 - <i>p</i> -Menthadiene | +67.0 |
| | +93.2 |

It will be observed that, in this case, the menthadiene has a much higher rotation than the menthenol from which it is produced by the elimination of water. Subsequently Fisher and Perkin (Trans., 1908, 93, 1872) resolved *dl*-1-methyl- Δ^1 -cyclohexene-4-carboxylic acid:



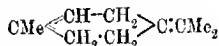
and prepared from the active acids, the menthenols (terpineols) and menthadienes (limonenes):



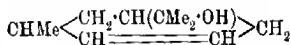
in the same way. Taking, as the example, the *l*-series, the following values were observed as the rotations of these substances:

| | |
|---|--------------|
| <i>l</i> -1-Methyl- Δ^1 -cyclohexene-4-carboxylic acid | $[\alpha]_D$ |
| Ethyl <i>l</i> -methylcyclohexenecarboxylate | -55° |
| <i>l</i> - Δ^1 - <i>p</i> -Menthenol(8) | -52 |
| <i>l</i> - Δ^1 : Δ^9 - <i>p</i> -Menthadiene | -46.6 |
| | -5.0 |

It is clear that the relationship between the values for the different substances given in this table are very similar to those shown in the preceding table, with the exception of the striking differences in the rotations of the menthadienes. It is well known that the active limonenes are somewhat easily racemised with formation of dipentene, and for this reason we were careful to conduct the elimination of water at the ordinary temperature with the aid of magnesium methyl iodide, and we were surprised to find that, instead of obtaining a hydrocarbon of higher rotation than the menthenol (terpineol) (*l*-limonene has $[\alpha]_D -120^\circ$), the rotation had decreased to -5° . No doubt this result was partly due to racemisation, because we were able to show that the substance contained considerable quantities of dipentene.* But it is very probable that the low rotation is also due to the hydrocarbon containing considerable quantities of terpinolene:



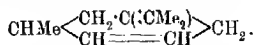
which is of necessity inactive. In the present communication it is shown that, when *d*- Δ^5 -*m*-menthenol(8) ($[\alpha]_D + 36.7^\circ$):



is digested with 6 per cent. oxalic acid, the resulting *d*- Δ^5 -*m*-menthadiene ($[\alpha]_D + 29.6^\circ$):



has a lower rotation than the menthenol instead of a higher one, as might have been expected from the experiments of Kay and Perkin just referred to. This would seem to indicate that this terpene may contain Δ^5 : Δ^8 -*m*-menthadiene:



and the rather high numbers obtained for the refractive power as the result of preliminary physical measurements seem to support this view. If this is the case, one of the asymmetrical carbon atoms of the menthenol will have disappeared during the formation of this substance by the elimination of water, and this may be the explanation of the drop in the rotation.

* As the presence of dipentene was only proved qualitatively, the statement (*loc. cit.*, p. 1873) that the hydrocarbon of $[\alpha]_D - 5^\circ$ consisted essentially of dipentene should not have been made, and is probably incorrect.

EXPERIMENTAL.

Preparation of 1-Methyl- Δ^5 -cyclohexene-3-carboxylic Acid and 1-Methyl- Δ^4 -cyclohexene-3-carboxylic Acid.

In the first experiments (*Trans.*, 1909, 95, 1897), the reduction of 5-hydroxy-*m*-toluic acid was carried out in *iso*amyl-alcoholic solution with sodium, but it was subsequently found that the acid is also reduced, although with some difficulty, when its solution in absolute alcohol* is treated with sodium. The pure acid, in quantities of 50 grams, dissolved in alcohol (1250 grams) was reduced by the rapid addition of sodium (180 grams) substantially in the manner described in detail in the case of the reduction of 4-hydroxy-*o*-toluic acid (*Trans.*, 1909, 95, 1876). After extracting in the usual way, the acid was reduced a second time under the same conditions, and in all about 1 kilogram of the hydroxy-acid was worked up, and yielded about 840 grams of reduction product. This acid (which consists for the most part of *trans*-1-methyleyclohexan-3-ol-3-carboxylic acid, compare *loc. cit.*, p. 1891), in quantities of 50 grams, was mixed with three volumes of fuming hydrobromic acid (saturated at 0°), and, after remaining for two days at the ordinary temperature, the liquid was heated on the water-bath for two hours, when it separated into two layers. The product was mixed with water, extracted twice with ether, and, after drying and evaporating, the crude bromo-acid was digested with alcohol (200 c.c.) and sulphuric acid (20 c.c.) for four hours on the water-bath, and then left for twenty-four hours. On adding water, the heavy bromo-ester was precipitated, and was extracted with ether, the ethereal solution was thoroughly washed with water and dilute sodium carbonate, carefully dried, evaporated, and the crude ester heated to boiling with three volumes of diethylaniline for eight hours. Excess of dilute hydrochloric acid was then added, the unsaturated ester extracted with ether, the ethereal solution washed first with dilute hydrochloric acid, and then with sodium carbonate, and distilled in steam.†

The volatile ester was extracted with ether, dried, and distilled, when almost the whole quantity passed over at 140–150°/100 mm., and weighed 710 grams. In order to avoid any possibility of intramolecular change (compare p. 2146), the hydrolysis of this ester was

* Distilled over calcium, see footnote, *Trans.*, 1909, 95, 1876.

† When all the unsaturated ester had passed over, a considerable amount of a solid, brown residue remained in the distilling flask. This was extracted with ether, and yielded on treatment with hydrogen bromide, diethylaniline, etc., exactly as described above, a further quantity of unsaturated ester, which was added to that obtained as the result of the first operation.

very carefully carried out. The ester was gradually mixed with exactly the quantity of alcoholic potassium hydroxide required for hydrolysis, the addition extending over about a week, and after remaining for ten days in all, at the ordinary temperature, water was added, and any non-hydrolysed ester extracted with ether. The aqueous solution was nearly neutralised with hydrochloric acid, saturated with carbon dioxide, evaporated until quite free from alcohol, acidified, and the unsaturated acids were extracted with ether and distilled, when almost the whole quantity passed over at $140\text{--}142^\circ/20\text{ mm.}$ It has already been mentioned (p. 2130) that this acid is a mixture of 1-methyl- Δ^5 -cyclohexene-3-carboxylic acid and 1-methyl- Δ^4 -cyclohexene-3-carboxylic acid, and, in order to separate these, the oil was digested with much water and excess of freshly precipitated calcium carbonate on the water-bath for several hours. After filtering and concentrating considerably, the calcium salt of the Δ^5 -acid separated as a voluminous mass of balls of needles, and the mother liquor, on concentration, deposited further crops of this same salt.

After a certain concentration had been reached, the brown mother liquors yielded a crop of calcium salt quite different in appearance from the calcium salt of the Δ^5 -acid. This salt was decomposed by hydrochloric acid, and the acid extracted, distilled under diminished pressure, and again made into calcium salt, and by repeating the process of fractional crystallisation, the two calcium salts were, as far as could be seen, completely separated.

dl-1-Methyl- Δ^5 -cyclohexene-3-carboxylic Acid.

In preparing this acid, the pure calcium salt, obtained in the way described in the last section, was decomposed by dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution washed, dried, and evaporated, and the acid distilled under diminished pressure:

0.1957 gave 0.4897 CO_2 and 0.1561 H_2O . $\text{C}=68.2$; $\text{H}=8.8$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C}=68.5$; $\text{H}=8.6$ per cent.

dl-1-Methyl- Δ^5 -cyclohexene-3-carboxylic acid is a rather viscous oil, which distils at $145^\circ/20\text{ mm.}$ or $177\text{--}180^\circ/100\text{ mm.}$, and, especially when warm, has a very unpleasant odour. The highly characteristic calcium salt appears to have the formula $(\text{C}_8\text{H}_{11}\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$:

0.1908 of the air-dried salt lost 0.0411 at 100° , and yielded

0.0627 CaSO_4 . $\text{H}_2\text{O}=21.54$; $\text{Ca}=9.67$.

0.1332 lost 0.0287 at 100° . $\text{H}_2\text{O}=21.54$.

0.1128 gave 0.0370 CaSO_4 . $\text{Ca}=9.65$.

$(\text{C}_8\text{H}_{11}\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=22.06$; $\text{Ca}=9.8$ per cent.

These analyses, for which I am indebted to Dr. A. N. Meldrum, were carried out with three different preparations of the salt.

Ethyl dl-1-Methyl-Δ⁵-cyclohexene-3-carboxylate.—This ester was prepared by warming the acid (15 grams) with alcohol (100 c.c.) and sulphuric acid (6 c.c.) for three hours on the water-bath. Water was then added, the ester extracted with ether, the ethereal solution washed with water and sodium carbonate, dried, evaporated, and the oil distilled under diminished pressure:

0.117 gave 0.2914 CO₂ and 0.0984 H₂O. C=71.2; H=9.8.

C₁₀H₁₆O₂ requires C=71.4; H=9.5 per cent.

This ester distils at 141–143°/100 mm., and possesses a penetrating and most unpleasant odour.

dl-Δ⁵-m-Menthenol(8) and dl-Δ⁵:8(9)-m-Menthadiene.

In preparing *dl-Δ⁵-m-menthenol(8)*, ethyl *dl-1-methyl-Δ⁵-cyclohexene-3-carboxylate* (10 grams) was added to an ethereal solution of magnesium methyl iodide containing 4 grams of magnesium, all rise of temperature above 25° being checked by cooling with water.

After twenty-four hours, the product was decomposed by the addition of water and then dilute hydrochloric acid, the ethereal solution washed well, dried, and evaporated, and the residue mixed with a solution of 2 grams of potassium hydroxide in methyl alcohol, and left for two days in order that any trace of unchanged ester might be removed. The neutral oil was then precipitated by water, extracted, and distilled under diminished pressure:

0.1515 gave 0.4319 CO₂ and 0.1604 H₂O. C=77.7; H=11.8.

C₁₀H₁₈O requires C=77.9; H=11.7 per cent.

dl-Δ⁵-m-Menthenol(8) distils at 115–117°/30 mm., and is a viscid, colourless oil, possessing a strong and pleasant odour of terpineol and peppermint. In order to convert this tertiary alcohol into the corresponding hydrocarbon, it was boiled with 6 per cent. aqueous oxalic acid in a reflux apparatus for three hours, then distilled in steam, and the distillate extracted with ether. After carefully drying over potassium carbonate and removing the ether by evaporation, the residual oil distilled almost completely at 72–180°, and two distillations over sodium yielded the pure terpene:

0.1192 gave 0.3834 CO₂ and 0.1282 H₂O. C=87.9; H=11.9.

C₁₀H₁₆ requires C=88.2; H=11.8 per cent.

dl-Δ⁵:8(9)-m-Menthadiene distils at 175–176°/765 mm., and has pronounced odour of lemons, which, however, is quite distinct from that of limonene.

Resolution of dl-1-Methyl- Δ^5 -cyclohexene-3-carboxylic Acid.

The resolution of this acid into its active modifications may be accomplished with the aid either of *l*-menthylamine or of quinine.

I. *Experiments with l-Menthylamine.*—The acid available for this purpose weighed rather more than 160 grams, and was divided into two parts. The oil (80 grams) was dissolved in 570 c.c. of *N*/10-sodium carbonate, heated to boiling, and mixed with a solution of pure *l*-menthylamine hydrochloride (120 grams), when a viscid syrup separated which soon began to crystallise. After remaining overnight, the aqueous liquid was decanted * from the semi-solid cake; the latter was then washed, and left in contact with porous porcelain until quite hard and dry; it then weighed 105 grams. The crude salt was rubbed with a little pure acetone in a mortar, quickly filtered, and the colourless residue crystallised from acetone, from which it separated in long, slender needles:

0.9028, made up to 20 c.c. with alcohol, gave $\alpha_D -0.48^\circ$ in a 2-dcm. tube at 16° , whence $[\alpha]_D -5.3^\circ$.

After two more crystallisations, the salt had $[\alpha]_D -2.8^\circ$, and after two further crystallisations, $[\alpha]_D -1.7^\circ$, and it therefore consists of the *l*-menthylamine salt of *d*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid:

0.1108 gave 5.1 c.c. N_2 at 18° and 760 mm. $N=5.3$.

$C_{12}H_{23}O_2N$ requires $N=4.7$ per cent.

By extracting the porous plates which had been employed in purifying the crude *l*-menthylamine salt as explained above, and carefully working up all mother liquors, about 120 grams of the pure *l*-menthylamine salt of rotation $[\alpha]_D -1.7^\circ$ were ultimately obtained, and this was decomposed by dilute sodium hydroxide, and after the *l*-menthylamine had been extracted with ether, the alkaline solution was acidified, the active acid extracted with ether, and distilled under diminished pressure:

0.1931 gave 0.4819 CO_2 and 0.1532 H_2O . $C=68.1$; $H=8.8$.

$C_8H_{12}O_2$ requires $C=68.5$; $H=8.6$ per cent.

d-1-Methyl- Δ^5 -cyclohexene-3-carboxylic acid boils at $145^\circ/20$ mm, and has the following rotation:

1.0088, made up to 20 c.c. with ethyl acetate, gave $\alpha_D +3.34^\circ$ in a 2-dcm. tube at 16° , whence $[\alpha]_D +33.1^\circ$.

Ethyl d-1-Methyl- Δ^5 -cyclohexene-3-carboxylate was prepared by mixing the acid (40 grams) with alcohol (200 grams) and sulphuric acid (15 c.c.), and, after remaining at the ordinary temperature for

* These aqueous liquors yield, on acidifying and extracting with ether, nearly 10 grams of acid, which was used in another experiment.

a week, water was added, and the oily ester extracted with ether. The ethereal solution was well washed with sodium carbonate, dried, and evaporated. The ester distilled at 140—141°/100 mm. as a mobile liquid with a penetrating and very unpleasant odour:

0.1856 gave 0.4849 CO₂ and 0.1626 H₂O. C=71.2; H=9.8.

C₁₀H₁₆O₂ requires C=71.4; H=9.5 per cent.

0.9520, made up to 20 c.c. with ethyl acetate, gave $\alpha_D + 2.91^\circ$ in a 2-dm. tube at 16.5°, whence $[\alpha]_D + 30.5^\circ$.

II. *Experiment with Quinine*.—This method of resolution, which appears to give good results, was, carried out subsequent to the experiments with *l*-menthylamine, just described, and with a comparatively small quantity of the *dl*-acid. The acid (45 grams) was digested in ethyl acetate solution with quinine (125 grams), and the clear solution left in the ice-chest for eight days, when a considerable quantity of a crystalline crust had separated. This was collected, twice recrystallised from ethyl acetate, and then decomposed in the usual manner, when it yielded an acid which distilled at 142°/20 mm., which had the following high rotation:

1.0632, made up to 20 c.c. with ethyl acetate, gave $\alpha_D + 3.31^\circ$ in a 2-dm. tube at 16°, whence $[\alpha]_D + 32.9^\circ$.

It would have been interesting again to have converted the active acid into the quinine salt in order to determine whether a higher rotation would have resulted than the $+33.1^\circ$ obtained in the case of the resolution with *l*-menthylamine, but unfortunately the acid was accidentally lost.

d-Δ⁵-*m*-Menthenol(8) and *d*-Δ^{5,8(9)}-*m*-Menthadiene.

The conversion of ethyl *d*-1-methyl-Δ⁵-cyclohexene-3-carboxylate into *d*-Δ⁵-*m*-menthenol(8) was brought about by adding the ester (15 grams) to an ethereal magnesium methyl iodide solution containing 6 grams of magnesium, the temperature being kept below 25° during mixing and subsequently. After twenty-four hours, the product was decomposed by water and hydrochloric acid in the usual manner, the ethereal solution washed well, dried, and evaporated. The residual oil distilled remarkably constantly at 115°/30 mm.:

0.1438 gave 0.4120 CO₂ and 0.1551 H₂O. C=78.1; H=12.0.

C₁₀H₁₆O requires C=77.9; H=11.7 per cent.

0.8810, made up to 20 c.c. with alcohol, gave $\alpha_D + 3.25^\circ$ in a 1-dm. tube at 16°, whence $[\alpha]_D + 36.7^\circ$.

d-Δ⁵-*m*-Menthenol(8) is a colourless, rather viscid oil, possessing a strong odour of terpineol and menthol; even when kept for several months, it showed no signs of crystallising, and an attempt to prepare a crystalline phenylurethane was also unsuccessful.

When a drop of sulphuric acid is added to the solution of this menthenol in acetic anhydride, a faint pink colour, like dilute permanganate, is produced, and, on keeping, this gradually becomes more violet and then fades. The menthenol (5 c.c.) was shaken with dilute sulphuric acid (350 c.c. of 5 per cent.) for seven days on the machine, the product distilled in a current of steam, and the volatile oil extracted and distilled under the ordinary pressure, when almost the whole quantity passed over at about 203° , and evidently consisted of the unchanged menthenol, only traces at most of the corresponding terpene having been produced. The solution in the steam distillation flask yielded, after saturation with ammonium sulphate and extraction with ether, about 0.5 gram of a syrup, which gradually crystallised and evidently consisted of the corresponding terpin, but the quantity was too small for purification. When the menthenol was mixed with three volumes of fuming hydrochromic acid (saturated at 0°), it did not appear to dissolve, and, even after several weeks, no solid additive product had been formed.

d- $\Delta^5:8^{(9)}$ -*m*-Menthadiene.—This terpene is formed when *d*- Δ^5 -*m*-menthenol(8) (10 grams) is digested with aqueous oxalic acid (100 c.c. of 6 per cent.) in a reflux apparatus for six hours, and the product distilled in a current of steam.

The volatile oil was extracted with ether, the ethereal solution dried very carefully, evaporated, and the residue distilled, when almost the whole passed over below 180° , and, after twice fractionating over sodium, the terpene distilled constantly at 175 – 176° :

0.1142 gave 0.3706 CO_2 and 0.1248 H_2O . $\text{C}=88.5$; $\text{H}=12.1$.

$\text{C}_{10}\text{H}_{16}$ requires $\text{C}=88.2$; $\text{H}=11.8$ per cent.

0.9124, made up to 20 c.c. with ethyl acetate, gave $\alpha_D + 2.71^{\circ}$ in a 2-dcm. tube at 17° , whence $[\alpha]_D + 29.6^{\circ}$.

1:1-Methyl- Δ^5 -cyclohexene-3-carboxylic Acid, 1- Δ^5 -*m*-Menthenol(8), and 1- $\Delta^5:8^{(9)}$ -*m*-Menthadiene.

The mother liquors from the separation of the *l*-menthylamine and quinine salts of *d*-1-methylcyclohexene-3-carboxylic acid were decomposed in the usual manner, and the acid (60 grams), which distilled at 142 – 146° and had $[\alpha]_D - 21.4^{\circ}$, was systematically treated with *l*-menthylamine and quinine, with the result that an acid was ultimately obtained which distilled at $142^{\circ}/20$ mm. and had the following rotation:

1.1009, made up to 20 c.c. in ethyl acetate, gave $\alpha_D - 3.41^{\circ}$ in a 2-dcm. tube at 15° , whence $[\alpha]_D - 30.9^{\circ}$.

It follows therefore that this acid is nearly pure 1:1-methyl- Δ^5 -cyclohexene-3-carboxylic acid, since the rotation of the corre-

sponding *d*-acid was found to be $+33.1^\circ$. Unfortunately no suitable crystalline salt of the *l*-acid was discovered, although experiments were made with *d*-hornylamine, *d*-isomenthylamine, and most of the usual alkaloids, and therefore complete separation could not be carried out.

Ethyl 1-1-Methyl- Δ^8 -cyclohexene-3-carboxylate, prepared from the acid by means of alcoholic sulphuric acid in the usual manner, distilled at $140-142^\circ/100$ mm.:

1.0090, made up to 20 c.c. with ethyl acetate, gave $\alpha_D - 2.78^\circ$ in a 2-dcm. tube at 15° , whence $[\alpha]_D - 27.4^\circ$.

This ester (27 grams) was added to an ethereal solution of magnesium methyl iodide containing 10 grams of magnesium, and, after remaining overnight, the product was decomposed by dilute hydrochloric acid in the usual manner, and yielded 22 grams of 1- Δ^8 -*m*-menthenol(8), which distilled at $104-105^\circ/20$ mm.:

0.1429 gave 0.4083 CO_2 and 0.1521 H_2O . C=77.7; H=11.8.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires C=77.9; H=11.7 per cent.

0.9986, made up to 20 c.c. with ethyl acetate, gave $\alpha_D - 32.5^\circ$ in a 2-dcm. tube at 17° , whence $[\alpha]_D - 32.6^\circ$.

The whole of this menthenol was hoiled with dilute oxalic acid (6 per cent.) for three hours, the product distilled in a current of steam, and fractionated, first under ordinary conditions, and then twice over sodium; the 1- Δ^8 -*m*-menthadiene thus obtained distilled at $175-176^\circ$, and had a strong odour of lemons:

0.1036 gave 0.3414 CO_2 and 0.1135 H_2O . C=88.1; H=11.9.

$\text{C}_{10}\text{H}_{16}$ requires C=88.2; H=11.8 per cent.

1.0021, made up to 20 c.c. with ethyl acetate, gave $\alpha_D - 2.58^\circ$ in a 2-dcm. tube at 16° , whence $[\alpha]_D - 25.3^\circ$.

Formation of the cis- and trans-Lactones of α -Methyl- γ -hydroxy-isopropyladipic Acid by the Oxidation of d- and 1- Δ^8 -m-Menthenol(8).

In carrying out this oxidation, *d*- Δ^8 -*m*-menthenol(8) (5 grams) was suspended in water and powdered ice (1 litre), and then a 1 per cent. solution of permanganate (13 grams) added in several portions, the whole being mechanically shaken after each addition. The slight excess of permanganate was removed by sodium sulphite, and, after heating on the water-bath and filtering, the filtrate and washings of the manganese precipitate were evaporated to a small bulk. The brown liquid was then rendered acid with dilute sulphuric acid, and further oxidised on the water-bath with potassium dichromate and sulphuric acid until action ceased. The product was saturated with ammonium sulphate and repeatedly

extracted with ether on the machine, the ethereal solution was dried and evaporated, and the syrupy residue esterified by boiling with 10 per cent. alcoholic sulphuric acid for twelve hours.

The ester was extracted with ether, the ethereal solution thoroughly washed with sodium carbonate, dried and evaporated, and the residue fractionated, when about two-thirds distilled at 188–190°/20 mm.:

0.1228 gave 0.2811 CO_2 and 0.0975 H_2O . $\text{C}=62.6$; $\text{H}=8.8$.

$\text{C}_{12}\text{H}_{20}\text{O}_4$ requires $\text{C}=63.2$; $\text{H}=8.8$ per cent.

1.0021, made up to 20 c.c. with alcohol, gave $\alpha_D - 1.88^\circ$ in a 2-dm. tube at 17°, whence $[\alpha]_D - 18.7^\circ$.

This ester was digested with dilute hydrochloric acid (3 per cent.) for several hours, evaporated to a small bulk, and the filtered liquid left over solid potassium hydroxide in a vacuum desiccator for some weeks, when the gummy mass gradually became semi-solid.

It was placed in contact with porous porcelain until quite colourless, and then several times crystallised from water, when a glistening mass of plates was obtained, which consisted of the lactone of *trans- α -methyl- γ -hydroxyisopropyladipic acid* * (compare p. 2132):

0.0907 gave 0.1999 CO_2 and 0.0657 H_2O . $\text{C}=60.1$; $\text{H}=7.9$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.0$; $\text{H}=8.0$ per cent.

0.1888, dissolved in water and titrated with $\text{N}/10\text{-NaOH}$, neutralised 9.5 c.c., whereas this amount of a monobasic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, should neutralise 9.4 c.c. A further 20.5 c.c. of $\text{N}/10\text{-NaOH}$ (making 30 c.c. in all) were then added, the solution heated to boiling, and titrated back, when it was found that the total neutralised was 19.2 c.c. The amount required for neutralisation on the assumption that the lactone-acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, had become dibasic by hydrolysis is 18.8 c.c.

The solution was concentrated, acidified, heated to boiling for a few seconds, and allowed to cool; it then rapidly deposited glistening plates of the *trans*-lactone. This lactone melts at 136°, and is readily soluble in warm water, but rather sparingly so in the cold; the hot saturated solution clouds on cooling, but rapidly crystallises if the sides of the vessel are rubbed with a glass rod.

It is remarkable that, although obtained from a strongly active ester simply by boiling with dilute hydrochloric acid, this lactone, as also the corresponding *cis*-lactone (see below), should be quite inactive.

The cis-Lactone.—The porous plates, used in the purification of the crude mixed lactones, were extracted with ether, the ethereal

* This substance has been provisionally named *trans*- in order to distinguish it from the more readily soluble modification of lower melting point which has been called *cis*-.

extract mixed with water and the aqueous mother liquors of the *trans*-lactone, and digested with carefully purified animal charcoal.

After filtering and evaporating to a small bulk, the solution was left over sulphuric acid, when it gradually deposited a mass of crystals, which were drained on porous porcelain and fractionally crystallised from water. In this way, a separation of the *trans*- and *cis*-lactones was ultimately accomplished.

The *cis*-lactone melts at about 102° , is readily soluble in warm water, and the concentrated solution clouds on cooling, as does that of the *trans*-lactone, and then deposits the lactone in glistening plates. On one occasion an aqueous solution, which had gradually concentrated in the air, deposited the *cis*-lactone in the form of a thick, glistening, prismatic crystal like a crystal of sugar. The analysis and titration of this lactone gave the following results:

0.1117 gave 0.2471 CO_2 and 0.0800 H_2O . $\text{C}=60.2$; $\text{H}=8.0$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.0$; $\text{H}=8.0$ per cent.

0.2090, dissolved in water, neutralised 10.4 c.c. of $N/10\text{-NaOH}$, whereas this amount of a monobasic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, should neutralise 10.45 c.c.

On boiling with an excess of sodium hydroxide and titrating back, it was found that 20.9 c.c. had been neutralised, which is exactly the amount the lactonic acid, after hydrolysis, should neutralise. The solution was concentrated, acidified, and boiled, when, on cooling, the lactone of melting point 102° crystallised out.

An exactly similar series of experiments were made on the oxidation of *l*- Δ^3 -*m*-menthenol(8), and as they yielded a similar ester, $\text{C}_{10}\text{H}_{16}\text{O}_4$, of rotation $[\alpha]_D +17.4^{\circ}$, which, on hydrolysis, was converted into the inactive *cis*- and *trans*-lactones of melting points 102° and 136° respectively, it is hardly necessary to give the details of these experiments.

dl-1-Methyl- Δ^1 -cyclohexene-3-carboxylic Acid, dl- Δ^1 -*m*-Menthenol(8),
and dl- Δ^1 :8(9)-*m*-Menthadiene.

The calcium salt of 1-methyl- Δ^1 -*m*-cyclohexenecarboxylic acid, obtained as explained on p. 2138, was decomposed with dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution dried and evaporated, and the residual viscid oil distilled under diminished pressure, when the whole quantity passed over at $143\text{--}146^{\circ}/20$ mm.:

0.1256 gave 0.3159 CO_2 and 0.0991 H_2O . $\text{C}=68.5$; $\text{H}=8.7$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C}=68.6$; $\text{H}=8.6$ per cent.

The constitution of this acid was proved by its conversion into methyl- Δ^1 -*m*-cyclohexene-3-carboxylic acid when boiled with alkalis,

an isomeric change which was brought about under the following conditions. The acid (8 grams) was digested with aqueous potassium hydroxide (50 c.c. of 30 per cent.) for four hours in a Jena-glass reflux apparatus, the solution was acidified, the acid extracted, dried, and left in contact with 30 c.c. of 8 per cent. alcoholic sulphuric acid at the ordinary temperature for fifteen hours. Water was then added, the oil extracted with ether, the ethereal solution washed with water, and then shaken with sodium carbonate in order to dissolve unesterified acid.* When the aqueous extract was acidified, an oily acid was deposited, which gradually crystallised, and this was collected and left in contact with porous porcelain until quite free from oil. The ester which had been produced yielded, on boiling with 30 per cent. potassium hydroxide and subsequent fractional esterification, a further quantity of the same solid (Δ^3) acid, and, when the operation was repeated a third time, a small quantity of solid acid was again obtained. Apparently a condition of equilibrium is established between the Δ^4 - and Δ^3 -acids during this process.

The solid acid was dissolved in sodium carbonate, digested with animal charcoal, again precipitated, and the colourless, crystalline mass, after remaining in contact with porous porcelain until quite dry, was analysed. Found, C=68.6; H=8.7. Calc., C=68.6; H=8.6 per cent.)

That this acid is 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid was proved by the melting point, 58–60°, and by the fact that, when mixed with some of this acid, which had been prepared by Perkin and Tattersall (Trans., 1905, 87, 1094) by another process, the mixture melted at the same temperature as the components. The identity was further proved by converting the acid into the dibromide (m. p. 165°) and hydrobromide (m. p. 108–109°; compare this vol., p. 2152).

Ethyl 1-Methyl- Δ^4 -cyclohexene-3-carboxylate.—This ester was prepared by digesting the acid (10 grams) with 6 per cent. alcoholic sulphuric acid (50 c.c.) for three hours, and, after the addition of water, extracting with ether in the usual way. It distilled at 142–144°/100 mm., and had a most unpleasant and penetrating odour.

This ester (10 grams) was added to an ethereal solution of magnesium methyl iodide, containing 4 grams of magnesium, and, after remaining for twenty-four hours, water was added and the

* This method of separation depends on the fact that 1-methyl- Δ^3 -cyclohexene-carboxylic acid is an $\alpha\beta$ -unsaturated acid, and is esterified with greater difficulty than 1-methyl- Δ^4 -cyclohexene-carboxylic acid, which contains the ethylene linking in the $\beta\gamma$ -position. The value of this process of separation will be discussed in detail in a subsequent communication.

product distilled in a current of steam. The distillate was extracted with ether, the ethereal solution dried and evaporated, and the Δ^4 -*m*-menthenol(8) distilled under diminished pressure, when it passed over at 115—117°/30 mm. as a viscid oil which had a strong odour of terpineol and menthol:

0.1145 gave 0.3267 CO_2 and 0.1224 H_2O . $\text{C}=77.8$; $\text{H}=11.9$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C}=77.9$; $\text{H}=11.7$ per cent.

$\Delta^{4:5(9)}$ -*m*-Menthadiene was obtained from Δ^4 -*m*-menthenol(8) by boiling with 6 per cent. aqueous oxalic acid exactly as described in the preparation of $\Delta^{5:8(9)}$ -*m*-menthadiene (p. 2139). It was purified by distillation in a current of steam and then twice over sodium, and boiled at 175—177°/757 mm.:

0.1347 gave 0.3358 CO_2 and 0.1452 H_2O . $\text{C}=88.2$; $\text{H}=11.9$.

$\text{C}_{10}\text{H}_{16}$ requires $\text{C}=88.2$; $\text{H}=11.8$ per cent.

The amount of these substances available was very small, and an attempt will be made to find a more satisfactory method for the preparation of 1-methyl- Δ^4 -cyclohexene-3-carboxylic acid in order, if possible, to prepare the active menthenols and menthadienes derived from it.

The author is indebted to Dr. A. N. Meldrum and Mr. L. Benson for preparing the 1-methylcyclohexan-5-ol-3-carboxylic acid required for this investigation, and to Miss B. Dobson for carrying out most of the analyses and determinations of refractive power.

The author also wishes to state that much of the heavy expense of this research was met by a grant from the Research Fund of the Royal Society.

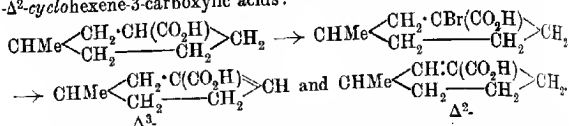
THE UNIVERSITY,
MANCHESTER.

CCXXIV.—*Experiments on the Synthesis of the Terpenes.*
Part XV. Δ^3 -*m*-Menthenol(8) and $\Delta^{3:8(9)}$ -*m*-Menthadiene.

By BERNARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar)
and WILLIAM HENRY PERKIN, jun.

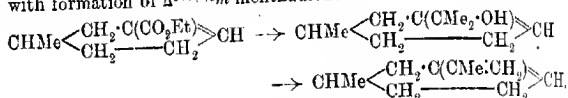
In a previous communication (Trans., 1905, 87, 1085), it was shown that 1-methylcyclohexan-3-carboxylic acid (hexahydro-*m*-toluic acid) is readily converted by bromination and subsequent

elimination of hydrogen bromide into a mixture of 1-methyl- Δ^3 - and Δ^2 -cyclohexene-3-carboxylic acids:

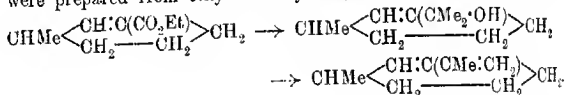


The separation of acids of such similar constitution proved to be a matter of much difficulty, and, as a result, only small quantities of the pure isomerides were available for subsequent investigation.

1-Methyl- Δ^3 -cyclohexene-3-carboxylic acid (m. p. 58–60°) was converted into its ester, and this, by the action of magnesium methyl iodide, into Δ^3 -*m*-menthenol(8), a substance which, when left in contact with a large excess of magnesium methyl iodide, loses water with formation of $\Delta^{3:8(9)}$ -*m*-menthadiene:

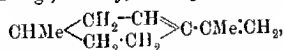


In a similar manner, Δ^2 -*m*-menthenol(8) and $\Delta^{2:8(9)}$ -*m*-menthadiene were prepared from ethyl 1-methyl- Δ^2 -cyclohexene-3-carboxylate:



It will be observed that $\Delta^{3:8(9)}$ - and $\Delta^{2:8(9)}$ -*m*-menthadiene contain conjugated double linkings, and investigation showed that these terpenes do, in fact, show the characteristic behaviour of substances which contain such groupings; they are, for example, only able to combine with two atoms of bromine or with one molecule of hydrogen chloride (compare *Trans.*, 1905, 87, 641, 667, and 1068).

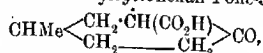
A short time since (this vol., p. 1428), Perkin and Wallach made a special study of another synthetical terpene which contains conjugated double linkings, namely, $\Delta^{3:8(9)}$ -*p*-methadiene:



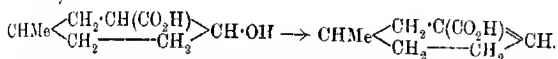
and observed that this terpene had a higher boiling point, density, and refractive index than terpenes, such as limonene, which do not contain conjugated double linkings (compare p. 2154), and it seemed desirable to investigate the physical constants of other terpenes of similar structure in order to determine whether this behaviour is a general one. The difficulty in preparing the *m*-menthadienes already mentioned in amount sufficient for accurate physical measurement is due to the difficulty in obtaining the 1-methyl-

cyclohexene-3-carboxylic acids in any considerable quantity by the process described at the beginning of this paper. An attempt was therefore made to devise a new method for the preparation of these acids, and this has been successful in the case of the Δ^3 -acid (m. p. 58–60°).

Quite recently (this vol., p. 1760), it was pointed out that 1-methyl-*cyclohexan-4-one* reacts readily with sodamide and carbon dioxide, with the formation of 1-methyl-*cyclohexan-4-one-3-carboxylic acid*:



and we have found that, under the conditions described in the present communication (p. 2150), the yield directly obtained is 50 per cent. of that theoretically possible.* When this acid is reduced with sodium amalgam, it yields 1-methyl-*cyclohexan-4-ol-3-carboxylic acid*, and this, on distillation, is almost quantitatively converted into 1-methyl- Δ^3 -*cyclohexene-3-carboxylic acid* (m. p. 58–60°):



This method of preparation is still laborious, but it is much less so than the original method, and it has now been found possible to prepare nearly 200 grams of the pure acid, of which part has been used in the present research, and the remainder is being resolved into its active constituents with the object of preparing and carefully investigating the corresponding active menthenols and menthadienes. In possession of sufficient material, we have now very carefully determined the physical properties of Δ^3 -*m*-menthenol(8) and $\Delta^{3:8(9)}$ -*m*-menthadiene (see pp. 2153, 2154).

We find that the values of Δ^3 -*m*-menthenol(8) show a remarkable similarity to those of Δ^3 -*p*-menthenol(8), and, when these numbers are compared with those of terpineol, it is seen that the proximity of the double linking to the $\cdot\text{CMe}_2\text{OH}$ group causes a fall of boiling point, density, and refractive index. Similarly, the values for $\Delta^{3:8(9)}$ -*m*-menthadiene are very like those of $\Delta^{3:8(9)}$ -*p*-menthadiene, but, when these values are compared with those of limonene, it is seen that the presence of conjugated linkings causes a considerable rise in boiling point, density, and refractive index.

A similar study of Δ^3 -*m*-menthenol(8) and of $\Delta^{3:8(9)}$ -*m*-menthadiene is in progress, and the results will shortly be ready for publication.

* It is actually considerably more, because a good deal of ketone is recovered unchanged and may be employed in a subsequent preparation.

EXPERIMENTAL.

Preparation of 1-Methylcyclohexan-4-one-3-carboxylic Acid and 1-Methylcyclohexan-4-ol-3-carboxylic Acid.

In order to obtain the large quantities of the above ketonic acid which we required for this research, we decided, as the result of a long series of comparative experiments, to modify the method of preparation originally employed (this vol., p. 1766) in the following way.

1-Methylcyclohexan-4-one (100 grams) is dissolved in dry ether (1 litre) in a three-necked flask fitted with a reflux condenser and mechanical stirrer, powdered sodamide (40 grams) is then added in lots of 10 grams, and the stirrer set in motion, when a rapid evolution of ammonia takes place. After the reaction has subsided, the mixture is heated on the steam-bath for an hour, allowed to cool, and then a stream of dry carbon dioxide passed through a wide tube so as to avoid stoppage, the whole being vigorously stirred during the operation. This causes a rise of temperature, and the passage of the gas is continued until the whole has cooled down to that of the atmosphere. The contents of the flask are then washed into a separating funnel with ice water, well agitated, the aqueous layer run off, and the ethereal solution kept in order to recover the unchanged ketone which it contains. The aqueous solution is acidified, extracted with ether, the ethereal solution shaken with sodium carbonate, and, after separating, the alkaline extract is cautiously treated with hydrochloric acid until the oily impurity has been completely precipitated and the crystalline acid commences to separate. After filtering, the filtrate is acidified with hydrochloric acid, and the colourless, crystalline precipitate of nearly pure 1-methylcyclohexan-4-one-3-carboxylic acid collected, washed, and drained on porous porcelain. The yield is 45–50 grams. The ethereal layer, containing the unchanged ketone, is washed, evaporated, and the residue distilled in a current of steam in order to separate it from a quantity of the bicyclic condensation product described on p. 2155. The ketone is extracted from the distillate, and, after one fractionation, is sufficiently pure for a further operation.

In preparing 1-methylcyclohexan-4-ol-3-carboxylic acid, 1-methylcyclohexan-4-one-3-carboxylic acid, in quantities of 10 grams, is dissolved in sodium carbonate, the solution made up to 600 c.c. with water, and treated, in a bottle fitted with a mechanical stirrer, with freshly prepared sodium amalgam (500 grams), which is added in three lots. Reduction takes place very slowly at the ordinary temperature, and the most suitable temperature appears to be

50–60°, which is maintained during the whole operation by placing the bottle in a trough of hot water; it is also necessary to neutralise the alkali produced by hydrochloric acid, which is dropped in in such a way that the liquid is always faintly alkaline.

The product is acidified with hydrochloric acid, saturated with salt, and extracted at least five times with much ether; the ethereal extract is dried over anhydrous sodium sulphate, and evaporated, when a syrup remains which soon becomes semi-solid, and the purification and properties of which have already been described (this vol., p. 1770).

1-Methyl- Δ^3 -cyclohexene-3-carboxylic Acid.

This acid has been prepared in large quantities in the following manner. Crude 1-methylcyclohexan-4-ol-3-carboxylic acid, obtained as described in the last section, is transferred to a distilling flask with a rather long neck, and heated in a metal-bath, when effervescence soon occurs, due to the decomposition of some unchanged ketonic acid. In a short time, water commences to be eliminated, and as soon as this and the ketone have ceased to pass over, the residue is distilled under diminished pressure, when almost the whole passes over at 155–160°/25 mm., and solidifies on cooling. The mass is left in contact with porous porcelain until free from traces of oily impurity; it then melts at about 57–58°, and is almost pure 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid. The yield is approximately 10 grams from 50 grams of the crude hydroxy-acid. For analysis, the substance was crystallised from formic acid, from which it separates in pearly plates, melting at 60°. (Found, C=68·4; H=8·6. Calc., C=68·6; H=8·6 per cent.)

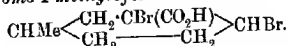
Careful comparison has shown that this acid is identical with the " Δ^1 -tetrahydro-*m*-toluic acid" obtained by Perkin and Fattersall (Trans., 1905, 87, 1092) by quite a different process. Ethyl 1-methyl- Δ^3 -cyclohexene-3-carboxylate, which has already been described (*loc. cit.*, p. 1094), was prepared in quantity by leaving the pure acid (50 grams) in contact with alcohol (300 c.c.) and sulphuric acid (30 c.c.) at the ordinary temperature for two days, and then heating on the water-bath for two hours.

After extracting in the usual way, it distilled at 146–148°/00 mm.

It was noticed that the $\alpha\beta$ -unsaturated acid is esterified with some difficulty at the ordinary temperature. Thus, for example, the mixture just mentioned, after being kept for twenty-four hours, contained a large amount of acid, and, even after forty-eight hours, considerable quantity of unesterified acid was still present. This behaviour has been utilised for separating the acid from the

isomeric β -acid by a process of fractional esterification (compare this vol., p. 2146).

3: 4-Dibromo-1-methylcyclohexane-3-carboxylic Acid,



In order to prepare this characteristic derivative, pure 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid, dissolved in a little dry chloroform, is cooled to -5° , and mixed with a few drops of dry bromine. At this low temperature, no action seems to take place, but, if allowed to rise to 15° , the colour of the bromine suddenly disappears, and then the addition of the theoretical amount takes place rapidly at 0° . During the operation a good deal of the dihydro-acid crystallises out, and the remainder is obtained by allowing the chloroform to evaporate. It is sparingly soluble in cold formic acid, and not very readily so on boiling, and separates in colourless, glistening leaflets:

0.3166 gave 0.3945 AgBr. Br = 53.0.

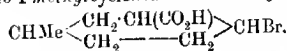
$\text{C}_8\text{H}_{12}\text{O}_2\text{Br}_2$ requires Br = 53.3 per cent.

When rapidly heated, 3: 4-dibromo-1-methylcyclohexane-3-carboxylic acid melts at 165° .

It dissolves readily in sodium carbonate, and the solution, on boiling, does not cloud with separation of the bromohydrocarbon, as sometimes happens in the case of $\alpha\beta$ -dibromo-acids of similar constitution. After boiling for ten minutes with a large excess of sodium carbonate, the solution deposited, on acidifying, a solid acid, which crystallised well from formic acid, melted at $148-150^\circ$, and appears to be a bromohydroxy-acid of the formula $\text{C}_7\text{H}_{11}\text{Br}(\text{OH})\cdot\text{CO}_2\text{H}$ (Found, Br = 32.7. Calc., Br = 33.2), but it was not further investigated.

The aqueous filtrate from this acid contains a considerable quantity of a syrupy acid which may be extracted with ether, and is probably the corresponding dihydroxy-acid.

4-Bromo-1-methylcyclohexane-3-carboxylic Acid,



1-Methyl- Δ^3 -cyclohexene-3-carboxylic acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and, on keeping, but more rapidly if slowly warmed to 70° , a syrup separates, which gradually crystallises. After washing with water and draining on porous porcelain, the substance was dissolved in a little warm formic acid, in which it is very readily soluble, and from which it separates in needles, melting at $107-109^\circ$:

0.1544 gave 0.1314 AgBr. Br = 36.2.

$C_9H_{13}O_2Br$ requires Br = 36.2 per cent.

This bromo-acid is decomposed by boiling with sodium carbonate, and the solution, on acidifying, deposits a crystalline precipitate of 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid.

Δ^3 -*m*-Menthenol(8) and $\Delta^{3,8(9)}$ -*m*-Menthadiene.

The conversion of ethyl 1-methyl- Δ^3 -cyclohexen-3-carboxylate into Δ^3 -*m*-menthenol(8) was carried out by adding the ester (13 grams) to an ethereal solution of magnesium methyl iodide; containing 6.5 grams of magnesium. After fifty hours, the product was decomposed by water (compare footnote, p. 2154), distilled in a current of steam, the distillate extracted with ether, and the ethereal solution dried, evaporated, and the residue distilled under diminished pressure. The whole quantity passed over at 114–117°/35 mm., and, after redistillation at 115°/35 mm., as a colourless, pleasant smelling, rather viscid liquid, and the yield of this pure Δ^3 -*m*-menthenol(8) was almost quantitative. The first time this substance was prepared (Trans., 1905, 87, 1100), it was noticed that much of the ethyl ester remained unattacked; this was due to the fact that the amount of magnesium (2.9 grams to 10 grams of ester) was too small, and the length of contact (twenty-four hours) was also not sufficient. Under the conditions mentioned above, only a trace of ethyl ester remained unchanged, and this was removed, before fractionation, by hydrolysis with a little methyl-alcoholic potassium hydroxide in the usual manner.

The phenylurethane of Δ^3 -*m*-menthenol(8) was prepared by leaving the menthenol with an equal volume of phenylcarbimide for three days. The mass was drained on porous porcelain, and then crystallised from 80 per cent. methyl alcohol, from which it separated in colourless needles, melting at 130°:

0.1057 gave 5.0 c.c. N_2 at 21° and 758 mm. N = 5.3.

$C_{17}H_{25}O_2N$ requires N = 5.1 per cent.

The physical properties of Δ^3 -*m*-menthenol(8) have been carefully determined, and found to be very similar to those of Δ^3 -*p*-menthenol(8) (compare Perkin and Wallach, this vol., p. 1435), as the following comparison shows:

| | $CH_3C \begin{array}{c} \text{CH}_2 \text{C}(\text{CH}_2\text{OH}) \\ \text{CH}_2 \end{array} - CH_2 - CH \cdot CH_3C \begin{array}{c} \text{CH}_2 \text{CH} \\ \text{CH}_2 \text{CH}_2 \end{array} \cdot C \cdot \text{CM}_2 \cdot \text{OH}$ | |
|-----------------------------|--|-------------|
| B. p. | 102°/14 mm. | 115°/35 mm. |
| d_{20}^{20} | 0.9263 | 0.9210 |
| n_D^{20} | 1.4798 | 1.4768 |
| M. | 47.10 (ole. 47.16) | 47.23 |
| M. p. of the phenylurethane | 130° | 128° |
| VOL. XCVII. | | 7 B |

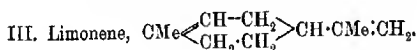
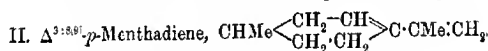
Δ^3 -*m*-Menthenol(8) has, so far, not crystallised, whereas Δ^3 -*p*-menthenol(8) is solid, and melts at 39°.

$\Delta^{3:8(9)}$ -*m*-Menthadiene has been prepared in two different ways, namely, (1) by the direct action of magnesium methyl iodide on ethyl 1-methyl- Δ^3 -cyclohexene-3-carboxylate, and (2) by the action of aqueous oxalic acid on Δ^3 -*m*-menthenol(8).

1. Ethyl 1-methyl- Δ^3 -cyclohexene-3-carboxylate (25 grams) was added to an ethereal solution of magnesium methyl iodide (10 grams of magnesium), and, after forty-eight hours, the product was decomposed by *dilute hydrochloric acid** and distilled in a current of steam. The ethereal extract of the distillate was dried, evaporated, and the product fractionated, when almost the whole passed over at 178—183°/750 mm., the amount of Δ^3 -*m*-menthenol remaining being very small.

The $\Delta^{3:8(9)}$ -*m*-menthadiene was then distilled three times over sodium, when it boiled constantly at 181—182°/760 mm.

2. Δ^3 -*m*-Menthenol(8) was boiled for three hours with 6 per cent. aqueous oxalic acid, and the product distilled in a current of steam. After extracting in the usual manner, it was found that the conversion into $\Delta^{3:8(9)}$ -*m*-menthadiene had been almost quantitative, and that this terpene again distilled at 181—182°/760 mm. The physical properties of both the specimens of this terpene were carefully determined, and found to be practically identical, and it is interesting to tabulate these (I) with those of the two following terpenes:



| | I. | II. | III. |
|------------------|----------|----------|----------|
| B. p. | 181—182° | 184—185° | 175—176° |
| d. 20°/20° | 0.8609 | 0.8580 | 0.8460 |
| n_D | 1.4975 | 1.4924 | 1.4746 |
| M. | 46.3 | 46.02 | 45.23 |

($\text{C}_{10}\text{H}_{16}$)⁻³ = 45.24.)

* The curious observation (compare p. 2153) has been made in this and in other cases, that the product of the action of magnesium methyl iodide on the ester of a methylcyclohexenecarboxylic acid, containing the double linking in the $\alpha\beta$ -position, yields the menthenol when it is treated with water, but the conjugated menthadiene when it is decomposed by *dilute hydrochloric acid*. In cases where the double linking is in any other position, this difference has not been observed, and the product has always been the menthenol whether the decomposition has been carried out simply by water or by the addition of hydrochloric acid.

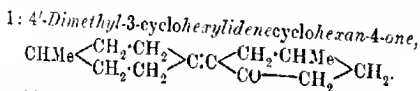
Cases I and II prove again that the effect of conjugation is to raise the boiling point, density, and refractive index above those of limonene. In possession of considerable quantities of pure 1,4,5,8-*m*-menthadiene, the authors have again investigated its behaviour with bromine and with hydrogen chloride (compare Trans., 1905, 87, 1101). The freshly distilled terpene (3.3588 grams) was dissolved in twice its volume of chloroform, cooled to -15° , and titrated with a solution of bromine in chloroform (1 in 3), when 12.6 c.c. were decolorised, the end-point being quite sharp, but a little hydrogen bromide was produced. This amount of terpene had therefore decolorised 4.2 grams of bromine, whereas the amount required for the formation of the tetrabromide, $C_{10}H_{16}Br_4$, is 8.0, and for the dibromide, $C_{10}H_{16}Br_2$, 4.0 grams. It is clear therefore, as had previously been pointed out, that this and other conjugated terpenes are only capable of combining with two atoms of bromine.

In investigating the action of hydrogen chloride, about 5 c.c. of the terpene were cooled to -15° , and a current of dry hydrogen chloride passed for one hour; the almost colourless product was left for two days, then placed over potassium hydroxide in a vacuum desiccator for several hours, and analysed:

0.1773 gave 0.1390 AgCl. Cl=19.4.

$C_{10}H_{16} \cdot HCl$ requires Cl=20.6 per cent.

It is therefore obvious that this conjugated menthadiene is only capable of combining with one molecule of hydrogen chloride.



Considerable quantities of this ketone, as well as higher condensation products of 1-methylcyclohexan-4-one, are produced during the action of sodamide and carbon dioxide (p. 2150). After extracting the sodium salt of 1-methylcyclohexan-4-one-3-carboxylic acid with water, the ethereal solution is evaporated, and the residue distilled in a current of steam, when unchanged methylcyclohexanone passes over, and the condensation products remain in the distilling flask. The dark brown oil is extracted with ether, the ethereal solution dried and evaporated, and the residue fractionated under diminished pressure, when a quantity of a pale yellow oil is obtained, which distils at $173-174^{\circ}/25$ mm., and has a pronounced fruity odour:

0.1971 gave 0.5862 CO_2 and 0.1924 H_2O . C=81.1; H=10.8.

$C_{14}H_{22}O$ requires C=81.5; H=10.7 per cent.
 $d_{20^{\circ}}/20^{\circ}=0.9728$; $n_D=1.4986$; M=62.1 (calc., 62.4).

This condensation product is very similar to the "bicyclic ketone," $C_{14}H_{22}O$, which Wallach (*Ber.*, 1896, **29**, 1595) obtained by the action of hydrogen chloride on 1-methylcyclohexan-3-one.

When a drop of sulphuric acid is added to the solution of the ketone in acetic anhydride, an intense crimson coloration is produced, which persists for a long time. The *oxime* was obtained by adding an aqueous solution of hydroxylamine hydrochloride to an alcoholic solution of the ketone, when, almost immediately, a crystalline precipitate began to form, which, after crystallisation from alcohol, was obtained in glistening needles, melting at 160° :

0.463 gave 26.4 c.c. N_2 at 18° and 758 mm. $N = 6.7$.

$C_{14}H_{23}ON$ requires $N = 6.3$ per cent.

THE UNIVERSITY,
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CCXXV.—*Studies in the Camphane Series. Part XXVIII. Stereoisomeric Hydrazones and Semicarbazones of Camphorquinone.*

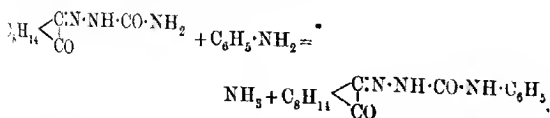
By MARTIN ONSLOW FORSTER and ADOLF ZIMMERLI.

THE expectation of stereoisomerism among semicarbazones is a natural corollary of the Hantzsch-Werner hypothesis. Up to the present time, however, it does not appear that any systematic attempt has been made to place the question of semicarbazone-isomerism on the basis occupied by that of the oximes. Apart from the distrust with which the hypothesis in question is still viewed in some quarters, the principal reason for this omission to bring the semicarbazones into line with oximes is the scattered and ill-defined nature of the evidence relating to the occurrence of isomerism in the former class. The cases of isothujone, carvenone, and tetrahydrocarvone appear to have been established by Wallach (*Ber.*, 1895, **28**, 1955), but the isomeric semicarbazones of citral and of ionone owe their formation to the existence of each ketone in two isomeric forms. Wallach has also shown that synthetic pulegone, obtained by condensation of methylhexanone with acetone, yields two semicarbazones (*Ber.*, 1896, **29**, 2955; also *Annalen*, 1898, **300**, 269), from both of which the ketone is regenerated by acid, but a claim for the production of isomerides from phenyl-1-methyl- Δ^6 -cyclohexen-5-one (Knoevenagel and Gold-

smith, *Ber.*, 1898, **31**, 2465) is not based on strong evidence. Benzoylmethylthiodiazole, on the other hand, gives rise to two derivatives (Wolff, *Annalen*, 1902, **325**, 173), but the supposed existence of two benzilmonosemicarbazones (Posner, *Ber.*, 1901, **34**, 3979) was shown to be fallacious by Biltz and Arnd (*Ber.*, 1902, **35**, 344; compare also Biltz, *Annalen*, 1905, **339**, 243), the second substance being 5:6-diphenyl-3-oxy-1:2:4-triazine, prepared by Thiele and Stange (*Annalen*, 1894, **283**, 27). Nef has recorded the production of two semicarbazones from propaldehyde (*Annalen*, 1904, **335**, 202), whilst Knoevenagel and Samel (*Ber.*, 1906, **39**, 681), and later Rupe and Dorschky (*Ber.*, 1906, **39**, 2112), found that when semicarbazide acts on carvone in the cold, the product is distinct from that described by von Baeyer, into which, however, it is convertible at raised temperatures.

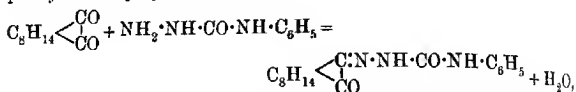
In reviewing the foregoing evidence relating to the existence of isomeric semicarbazones, we have not encountered any systematic attempt to explain the phenomenon, but the experiments described in this paper lead us to express the opinion that stereoisomerism of the type displayed by oximes must now be regarded as existing in this class also.

Our attention was drawn to the subject by an observation made in connexion with camphorquinonesemicarbazone (Lapworth and Chapman, *Trans.*, 1901, **79**, 381), and our thanks are due to Dr. Lapworth for his consent to our using this material. In preparing it by the slightly modified process of Diels and vom Dorp (*Ber.*, 1903, **36**, 3190), we noticed that the mother liquor contained a more soluble isomeride melting at a lower temperature than the modification already described, and calling the latter the α -semicarbazone, we refer to the new compound as the β -semicarbazone. When this is heated above its melting point, it is converted into the α -semicarbazone, and the latter, under the influence of hot aniline, undergoes the change described by Borsche (*Ber.*, 1901, **14**, 4297; 1904, **37**, 3177), giving rise to camphorquinonephenylcarbamylhydrazone, with liberation of ammonia:



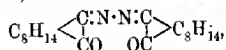
The product, however, is an equilibrium mixture of two isomerides, related to one another in a manner similar to the connexion between the semicarbazones. Both camphorquinonephenylcarbamylhydrazones are produced, also, when the β -semicarbazone is heated

with aniline, and by the condensation of camphorquinone with phenylcarbamyldiazide:

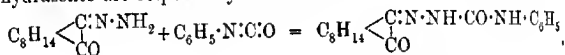


and they may be obtained separately by the action of phenylcarbimide on two new hydrazones of camphorquinone.

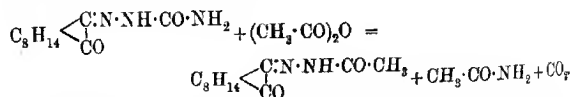
The action of hydrazine on camphorquinone is stated by Oddo (*Gazzetta*, 1897, **27**, ii, 117) to yield "biscamphanonazine," identical with Angeli's azocamphanone (*Gazzetta*, 1894, **24**, ii, 44), produced in association with camphenone by heating diazocamphor. As represented by Angeli, the formation of azocamphanone:



obviously depends on the condensation of hydrazine with two molecules of the diketone, but we find that if the substances interact in molecular proportion, two new derivatives of camphorquinone are produced; these, being isomeric, are referred to as the α - and β -hydrazones, and it is by the action of phenylcarbimide on these two substances that the above-mentioned α - and β -phenylcarbamyldhydrazones are respectively obtainable:

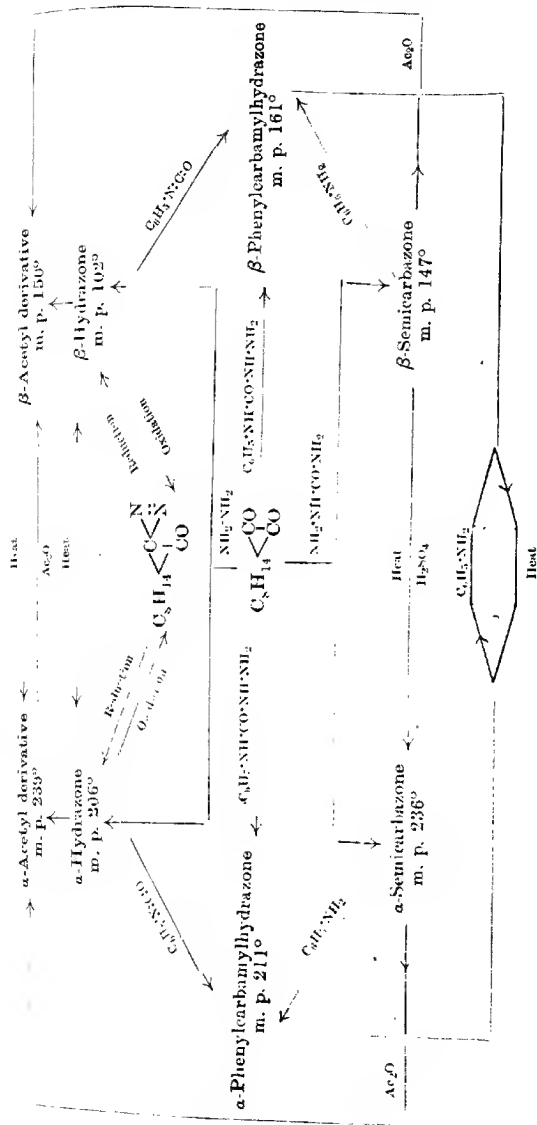


Thus, the isomeric hydrazones (m. p. 206° and 102°) are connected through the isomeric phenylcarbamyldhydrazones (m. p. 211° and 161°) with the isomeric semicarbazones (m. p. 236° and 147°) respectively, and the members of each pair bear to one another the same relation in respect of solubility, fusibility, and interconvertibility by heat. A further connexion between the hydrazones and semicarbazones is established by the fact that whilst acetic anhydride converts the hydrazones into acetyl derivatives (m. p. 239° and 150°), of which the β -compound is transformed into the α -modification by heat, an equilibrium mixture of these isomeric acetyl derivatives follows the action of hot acetic anhydride on the isomeric semicarbazones:



These reactions are summarised in the diagram on p. 2159.

It now becomes necessary to explain our grounds for ascribing the present case of isomerism to stereochemical rather than struc-

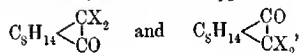


tural considerations, and since the only justification for a stereochemical explanation is the exclusion of structural differences, we proceed to deal with the possible causes of the foregoing relationships. These are:

1. Dimorphism, condemned by the distinct differences in optical activity which solutions of the respective pairs display under comparable conditions.

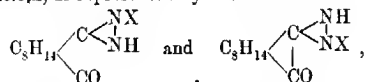
2. Polymerism, which might be suspected from the higher melting point and sparing solubility of the α -compounds. The latter property has precluded application of the freezing-point method of molecular-weight determination except in the case of the α -phenyl-carbamylhydrazone; this is normal, and so is the α -semicarbazone in boiling chloroform, whilst for other reasons which become apparent later in this paper it is difficult to believe that the less fusible member of each pair is merely a polymeride of the corresponding β -modification.

3. The structural difference which, depending on the asymmetry of the camphane molecule, renders the types,

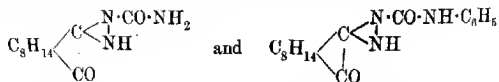


distinct from one another. The principal objection to this explanation is one which is familiar to all workers with camphor derivatives, namely, the immensely superior reactivity of the α -position. But it is excluded also by the formation of the hydrazones on reducing diazocamphor, supported by the improbability of the above types undergoing interconversion by merely heating the substances at 100–200°.

4. *cis-trans*-Isomerism, also depending on the asymmetry of the camphane nucleus, as represented by the formulæ:

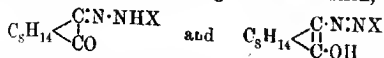


the possibility of which has been indicated by Armstrong and Robertson (Trans., 1905, 87, 1278). This point would be difficult to argue in the case of the semicarbazones and phenylcarbamylhydrazones if these had the constitution:

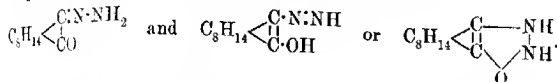


respectively, but is simplified by their experimental relation to the hydrazones, because it is obvious that *cis-trans*-isomerism of the order shown above could not occur in the case of the latter substances.

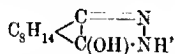
5. The structural difference arising from enolisation, namely:



as suggested by Betti in connexion with the phenylhydrazones (Ber., 1899, **32**, 1995). Here again the test is furnished by the simple hydrazones, which would be represented as:

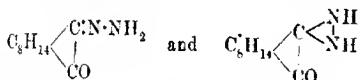


But this enolic formula represents the nitrogen in a condition hopelessly unprotected and quite incompatible with stability, whilst the alternative cycloid could not reasonably be expected to display chemical behaviour practically identical with the azethenoid compound represented by the first of the above expressions. The latter remark applies also to the formula:

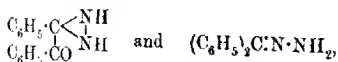


suggested by analogy to Hantzsch's representation of the alkali derivatives from oximinoketones. Thus the keystone of the discussion is the constitution of the simple hydrazones.

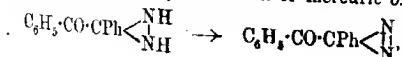
6. The structural difference of compounds derived from the azethenoid and cyclic hydrazones:



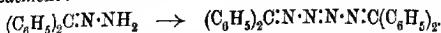
respectively. The discussion of this possibility involves a reference to the early work of Curtius on the interaction of hydrazine hydrate and ketonic substances. In dealing with the constitution of hydrazine derivatives from benzil and benzophenone, Curtius and Thun (*J. pr. Chem.*, 1891, [ii], **44**, 161) and, later, Curtius and Rautenberg (*loc. cit.*, p. 192) distinguish the products by the formulae:



respectively. Their principal reasons for doing so were the superior reactivity of the benzophenone derivative towards benzaldehyde, although the benzilhydrazone also condenses with that substance, and the oxidation of the benzilhydrazone to the corresponding derivative of diazomethane by the action of mercuric oxide:

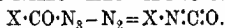
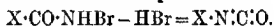


the benzophenonehydrazone being stated to yield a tetrazone by this treatment:



The evidence of tetrazone-formation will be found on examination, however, to be noticeably slender, and in the light of our own experiments we suggest that the "tetrazones" derived from benzophenonehydrazone (Curtius and Rautenberg, *loc. cit.*), benzylidenehydrazone (Curtius and Pflug, *loc. cit.*, p. 535), and acetophenonehydrazone (Curtius and Pflug, *loc. cit.*) are unstable derivatives of diazomethane, corresponding with that obtained from benzylhydrazone.

If this suggestion is justified it would, at first sight, appear to confirm the cyclic representation of the hydrazones. But it has been already pointed out that *cis-trans*-isomerism of an unsubstituted cyclic hydrazone does not seem possible, and the direct consequence of revealing isomerism in a simple hydrazone is therefore to discredit the cyclic structure for at least one member of the pair in favour of the azethenoid representation. How, then, is the formation of a diazomethane derivative from an azethenoid hydrazone to be explained? We suggest the following interpretation, first pointing out that it is probably the self-evidence of the conclusion that a hydrazone, convertible into a diazomethane derivative by mercuric oxide, must be derived from a cyclic type, which has obscured the possibility of an alternative explanation. It seems to us most likely that the cause of this change is to be found in the Hofmann-Curtius reaction, which, without quoting other examples (Trans., 1909, 95, 433; Schroeter, *Ber.*, 1909, 42, 2336) may be summarised in the equations:



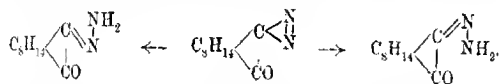
Applying this to the present question, we have to deal with a case of arrested transformation:



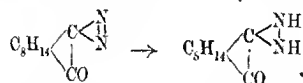
it being impracticable for the denuded atom of nitrogen to displace carbon from its position in the molecule, with the result that the azethenoid linking incurs a redistribution of valency.

Although a superficial criticism of this explanation might dismiss it as forced, and less probable than the one at present accepted, it is strongly supported by the following circumstances. As already pointed out, the isomeric camphorquinonehydrazones cannot both have the cyclic structure; if, on the other hand, one were cyclic and the other azethenoid, some difference in behaviour towards an oxidising agent should evince itself. But there is none. The

α - and β -hydrazones, dissolved in cold pyridine, have been oxidised with aqueous mercury acetamide to diazocamphor, and the precipitation of mercury takes place instantaneously in both cases. Moreover, by reducing diazocamphor in cold alcohol with ammonium sulphide, both hydrazones have been regenerated. It appears to us that these experiments point incontestably to stereoisomerism of the Hantzsch-Werner type. Theoretical considerations make it clear that at least one of the hydrazones must be azethenoid, and since oxidation of both leads to diazocamphor, the production of a diazomethane derivative from a hydrazone by this step cannot be accepted any longer as evidence of the cyclic structure. Furthermore, the fact that diazocamphor yields both hydrazones on reduction vitiates the conclusion that because diazomethane is cycloid, a hydrogenised diazocamphor must be a cyclic hydrazone. On the other hand, formation of both hydrazones on reducing diazocamphor gives colour to our hypothesis, because if it be admitted that ring-scission occurs on reduction, *anti*- and *syn*-modifications would be produced simultaneously:



Moreover, from relationships developed recently between structure and optical activity in the camphane series (Trans., 1909, 95, 942), it is to be expected that a substance derived from diazocamphor in the manner indicated by the formulæ:

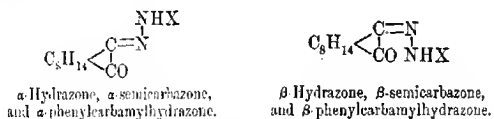


would display lower rotatory power than diazocamphor itself, whereas the α - and β -hydrazones of camphorquinone both have distinctly higher molecular rotation. Furthermore, they do not differ greatly from one another in respect of this property, although a considerable difference might be anticipated between an azethenoid and a cyclic hydrazone.

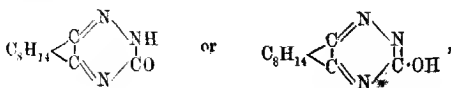
The second chemical distinction which has been mentioned as leading Curtius to differentiate between cyclic and azethenoid hydrazones, namely, condensation with benzaldehyde, corroborates the evidence from oxidation. When suspended in cold water and shaken with this agent, both hydrazones undergo immediate condensation, indicated by a change of colour, since the heuzylidene derivative is deep yellow. The final product is the same whether the α - or the β -hydrazone is employed as starting-material, but the

deeper colour generated by the latter substance, and the delay in solidification shown by the product, suggest the preliminary formation of an unstable β -benzylidene compound.

Before concluding, we ought to mention that there is one distinction existing between the members of each pair which will doubtless be quoted as evidence in conflict with our explanation. It is a fact that whilst the α -hydrazone, α -semicarbazone, and α -phenylcarbamylhydrazone are colourless, the β -modifications are faintly yellow. It was by a distinction of this order that Armstrong and Robertson (*loc. cit.*) attempted to justify their representation of the phenylmethylhydrazone and phenylbenzylhydrazone of camphorquinone as "phanes," whilst retaining the azethenoid structure for the diphenylhydrazone, and if the same principle were applied to the substances described herein, the colourless α -hydrazones and its derivatives would be represented as cycloid, whilst the yellow β -compounds would be labelled azethenoid. In the foregoing remarks we have endeavoured to show that this cannot be accepted, but even if that evidence could be swept aside, we still hold that the conclusion from colour is in support of our hypothesis, which regards the α - and β -derivatives as *anti*- and *syn*-carbonylic respectively:



For it cannot be denied that from the conflict of views as to the relation between colour and constitution there does emerge this principle, that colour appears to be associated with a concentration of unsaturated atoms. Clearly there is a more intimate massing of such atoms in the β -compounds as represented above than in their isomerides, and it is fair to claim this point as favouring the stereochemical hypothesis. In further support of the latter, it may be stated that the only chemical distinction between the members of each pair which has yet come to light is to be found in the behaviour of the semicarbazones towards aqueous alkali. Whilst the α -semicarbazone forms a yellow solution which does not undergo spontaneous alteration, the dissolved β -semicarbazone quickly loses its colour, and on acidifying the liquid there is liberated the oxytriazine:



production of which is obviously more favoured by the *syn*-carbonylic configuration than by the alternative one.

These, then, are our principal reasons for inclining to the stereochemical representation of the camphorquinonehydrazones and their derivatives described in this paper. If this interpretation finds acceptance, it carries with it fresh evidence in support of the Hantzsch-Werner hypothesis.

EXPERIMENTAL.

Action of Hydrazine Hydrate on Camphorquinone.

Azocamphanone.—Twelve grams of hydrazine hydrochloride, dissolved in 100 c.c. of water, were treated with 12 grams of potassium hydroxide, and, when cold, mixed with 33 grams of camphorquinone in 100 c.c. of hot alcohol. During one hour at 40° the appearance of the liquid had completely changed, owing to the separation of a bulky, pale yellow precipitate; this was collected, washed with 50 per cent. alcohol, and found to weigh 29 grams. The product was dissolved in 400 c.c. of boiling alcohol, which deposited lustrous, six-sided, transparent plates, almost rhombohedral in form; becoming deep yellow at 195°, it melted and decomposed at 218°. (Found, $N = 8.75$; $C_{20}H_{22}O_2N_2$ requires $N = 8.53$ per cent.) This compound is the "azocamphanone" of Angeli (*loc. cit.*), who records 222° as the melting point, whilst Oddo gives 217–218°. It does not reduce hot Fehling's solution, and is not hydrolysed by a hot 20 per cent. solution of alcoholic potassium hydroxide; concentrated hydrochloric acid, however, when mixed with an alcoholic solution and boiled, eliminates hydrazine, but cold concentrated sulphuric acid, although forming a deep yellow solution, does not resolve azocamphanone into hydrazine and camphorquinone. An alcoholic solution does not change when heated with an aqueous solution of mercury acetamide.

When powdered or in separate crystals, azocamphanone appears colourless, but when viewed in bulk it has a yellow tinge, and solutions are deep yellow; 0.3104 gram, dissolved in chloroform and made up to 25 c.c., gave α_D^{20} in a 2-dm. tube, whence $[\alpha]_D^{20} 174.5^\circ$ and $[M]_D^{20} 571^\circ$, not 790° , as previously stated in error (Trans., 1909, 95, 948).

The Isomeric Camphorquinonehydrazones, $C_{20}H_{22}N_2O_2$.—An aqueous solution of hydrazine hydrate prepared from 30 grams of hydrazine sulphate and 24 grams of potassium hydroxide in 150 c.c. of water was mixed with 33 grams of camphorquinone, dissolved in 150 c.c. of hot alcohol. After three hours at 40°,

23 grams of pale brown crystals had separated, quite distinct in appearance from the bulky precipitate of azocamphanone, and a current of steam having been passed through the filtrate until all volatile matter was removed, a further 2 grams crystallised from the hot liquid, so that under these conditions the yield of α -hydrazone amounted to 75 per cent. There was not any azocamphanone or camphorquinone, and after recrystallisation from about 400 c.c. of boiling alcohol, the α -hydrazone separated in long, lustrous, transparent prisms, melting and evolving gas at 200° :

0.2538 gave 0.6189 CO_2 and 0.2037 H_2O . $\text{C} = 66.51$; $\text{H} = 8.98$.

0.1418 „ 18.9 c.c. N_2 at 15° and 751.5 mm. $\text{N} = 15.43$.

$\text{C}_{10}\text{H}_{16}\text{ON}_2$ requires $\text{C} = 66.66$; $\text{H} = 8.88$; $\text{N} = 15.55$ per cent.

The α -hydrazone and its solutions are colourless, but large crystals frequently have a brown tinge; 0.3110 gram, dissolved in chloroform and made up to 25 c.c., gave α_D $7^{\circ}9'$ in a 2-dcm. tube, whence $[\alpha]_D$ 287.4° . The compound is insoluble in petroleum, and is not readily soluble in other media even when these are boiled; acetone or benzene is a convenient solvent from which to obtain it in colourless crystals, but upwards of 100 c.c. of the latter solvent at the boiling-point are required to dissolve 1 gram of the substance. It is readily soluble, however, in warm phenol, and sparingly so in cold pyridine.

A solution in chloroform decolorises bromine immediately, and ammoniacal silver oxide is reduced when warmed with the alcoholic solution. On adding solid sodium nitrite to a cold suspension of the α -hydrazone in glacial acetic acid, the salt assumed a transient purple tint, whilst the liquid became yellow and evolved gas; on diluting the acetic acid with water, azocamphanone was precipitated.

On passing a current of steam through the filtrate from the α -hydrazone as prepared under the foregoing conditions, 3 grams of a straw-yellow, crystalline material were carried over. The yield of this compound, however, was trebled by adding 40 grams of hydrazine hydrate to 50 grams of camphorquinone dissolved in 75 c.c. of alcohol, when the deep yellow colour changed immediately to pale brown; copious precipitation of the α -hydrazone took place after a very short interval, and at the end of half an hour the liquid was filtered and subjected to a current of steam. The solid distillate, consisting of β -hydrazone, weighed 12.5 grams, whilst 2 grams more were obtained by extracting the distilled water (1200 c.c.) with ether; the yield of accompanying α -hydrazone was 66.6 per cent., and if both compounds are required, the above conditions of procedure are the most economical. The β -hydrazone was recrystallised twice from boiling petroleum (b. p. $60-80^{\circ}$), 12 grams requiring 120 c.c. of the solvent, which deposited long,

lustrous, straw-yellow needles or transparent prisms, melting at 102° :

0.2038 gave 0.4975 CO_2 and 0.1632 H_2O . $\text{C}=66.59$; $\text{H}=8.96$.

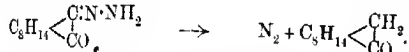
0.1864 „ 26.6 c.c. N_2 at 25° and 754 mm. $\text{N}=15.79$.

$\text{C}_{10}\text{H}_{16}\text{ON}_2$ requires $\text{C}=66.66$; $\text{H}=8.88$; $\text{N}=15.55$ per cent.

The substance has a faint odour suggesting that of bornylamine; it is readily soluble in organic media, excepting petroleum. A solution containing 0.3134 gram, made up to 25 c.c. with chloroform, gave $\alpha_D^{20} 5.48'$ in a 2-dcm. tube, whence $[\alpha]_D^{20} 231.3^{\circ}$. An alcoholic solution reduces cold ammoniacal silver oxide, and a solution in chloroform decolorises bromine immediately.

Interconversion of the Hydrazones.

On melting the β -hydrazone, it was noticed that if the temperature of the bath is raised to 150 – 160° the liquid solidifies, and this change was found to be due to conversion into the isomeride, which is readily isolated by recrystallisation from hot alcohol. The converse transformation cannot be brought about by merely melting the α -hydrazone, because this modification slowly loses nitrogen at 205 – 210° , yielding camphor:



If, however, the α -hydrazone is dissolved in molten paraffin wax, and maintained at 180° during a few minutes, it is a simple matter to demonstrate the formation of the β -hydrazone by suspending the product in hot water, and passing a current of steam through the liquid, when the volatile modification is carried into the condenser.

Action of Sulphuric Acid on the Hydrazones.

The hydrazones behave exactly alike towards sulphuric acid. When covered with the warm agent of 30 per cent. strength, a clear solution is formed almost immediately, and this at once becomes turbid, setting to a paste of azocamphanone in the course of a few minutes; on extracting the filtered product with boiling alcohol, crystals of hydrazine sulphate remain undissolved. With 10 per cent. acid, a clear solution is not produced, because the dissolution of the hydrazone is overtaken by the separation of azocamphanone.

Acyl Derivatives of the Hydrazones

The α -Formyl Derivative, $C_8H_{14} \begin{smallmatrix} \diagup \\ C \cdot N \cdot NH \cdot CHO \\ \diagdown \\ CO \end{smallmatrix}$.—On dissolving

1 gram of the α -hydrazone in 10 grams of formic acid (D 1.2), the pale yellow solution remained clear during a few seconds, when a shower of crystals separated; the derivative was recrystallised from boiling alcohol, of which about 70 c.c. were required by 1 gram, and was deposited in colourless, lustrous, six-sided plates, which displayed frequent twinning. It melts at 234° :

0.1240 gave 14.6 c.c. N_2 at 18° and 757 mm. $N=13.54$.

$C_{11}H_{16}O_2N_2$ requires $N=13.45$ per cent.

The formyl derivative is insoluble in boiling petroleum, and dissolves sparingly in methyl alcohol, benzene, acetone, and chloroform unless these solvents are heated, 15 c.c. of the last-named, for example, dissolving about one decigram until warmed; it is more readily soluble in pyridine and glacial acetic acid. A solution containing 0.1720 gram, made up to 25 c.c. with chloroform, gave $\alpha_D^{20} 3.33'$ in a 2-dm. tube, whence $[\alpha]_D^{20} 258.0^\circ$. On adding ferric chloride to an alcoholic solution, a pale brown coloration is developed, whilst that with copper acetate is grass-green. Aqueous alkalis dissolve the substance readily, producing a bright yellow solution, and on adding ferrous sulphate to the diluted liquid a dark bluish-green precipitate is formed; when the alkaline solution is left at the laboratory temperature, the colour quickly fades, and the α -hydrazone separates.

The same formyl derivative was also produced by the action of the acid on the β -hydrazone. An attempt to prepare a benzoyl derivative by the action of benzoyl chloride on the formyl compound dissolved in pyridine was not successful.

The α -Acetyl Derivative, $C_8H_{14} \begin{smallmatrix} \diagup \\ C \cdot N \cdot NH \cdot CO \cdot CH_3 \\ \diagdown \\ CO \end{smallmatrix}$.—Although

dissolving readily in cold formic acid, the α -hydrazone is only moderately soluble in cold glacial acetic acid; it dissolves on warming the liquid, but does not crystallise readily even on dilution, owing to partial acetylation. The substance was therefore warmed with five parts of acetic anhydride, when the acetyl derivative separated as a paste of crystals at the moment of complete dissolution in the hot liquid; recrystallisation from a considerable proportion of boiling alcohol gave long, lustrous, snow-white needles, melting and decomposing at 239° :

0.1047 gave 11.8 c.c. N_2 at 17° and 760 mm. $N=13.07$.

$C_{12}H_{18}O_2N_2$ requires $N=12.61$ per cent.

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A solution containing 0.2226 gram, made up to 20 c.c. with chloroform, gave α_D 5°54' in a 2-dcm. tube, whence $[\alpha]_D$ 265.5°. The compound dissolves freely in dilute aqueous alkali, developing a bright yellow coloration, and the solution yields an intense bluish-green precipitate with ferrous sulphate; 0.2083 gram, dissolved in 5 c.c. of 10 per cent. sodium hydroxide and diluted to 25 c.c. with water, gave α_D 4°12' in a 2-dcm. tube, whence $[\alpha]_D$ 252.0°. In process of time, the colour of the alkaline solution fades, and the α -hydrazone separates from the liquid.

The β -Acetyl Derivative.—On dissolving the β -hydrazone in five parts of cold acetic anhydride, the temperature rose slightly, and long, flat, transparent prisms began to separate in the course of a few minutes; after recrystallisation from boiling petrolcum, the substance was found to be pale yellow, and melted at 150°:

0.1297 gave 14.5 c.c. N_2 at 18° and 760 mm. $N = 12.91$.

$C_{13}H_{18}O_2N_2$ requires $N = 12.61$ per cent.

A solution containing 0.3890 gram, made up to 25 c.c. with chloroform, gave α_D 6°58' in a 2-dcm. tube, whence $[\alpha]_D$ 223.8°. The solution in aqueous alkali has the same appearance as that of the α -acetyl derivative, developing a similar precipitate with ferrous sulphate; in the course of some hours, the yellow colour fades, and the liquid deposits crystals of the α -hydrazone.

When the β -acetyl derivative is heated at temperatures above its melting point, varying proportions of the α -acetyl compound are produced, but the conversion is not complete; moreover, on heating the α -acetylhydrazone in acetic anhydride, a certain amount of the β -isomeride may be isolated from the product.

The α -Benzoyl Derivative, $C_8H_7 \begin{smallmatrix} \diagup C:N \cdot NH \cdot CO \cdot C_6H_5 \\ \diagdown CO \end{smallmatrix}$.—The α -hydrazone requires about 25 parts of pyridine to maintain a clear solution at zero, and on adding the calculated amount of benzoyl chloride, also dissolved in ice-cold pyridine, the hydrochloride of the base separated, the benzoyl derivative being precipitated on dilution with water; recrystallisation from boiling alcohol, in which it is sparingly soluble, gave tough, lustrous, snow-white needles, becoming yellow above 200°, and melting at 219–222°, according to the rate at which the temperature is raised:

0.1322 gave 11.4 c.c. N_2 at 16° and 757 mm. $N = 10.01$.

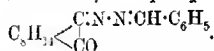
$C_{17}H_{20}O_2N_2$ requires $N = 9.86$ per cent.

The substance is not readily soluble in chloroform, and a solution containing 0.2135 gram, made up to 50 c.c. with this solvent, gave α_D 1°45' in a 2-dcm. tube, whence $[\alpha]_D$ 204.9°. Although in part dissolved by 2 per cent. aqueous sodium hydroxide, the benzoyl derivative did not form a clear solution; 0.1904 gram, suspended

in about 20 c.c. of the agent, was made up to 50 c.c. with absolute alcohol, the clear, deep yellow liquid giving α_D $1^\circ 50'$ in a 2-dcm. tube, whence $[\alpha]_D$ 240.7° .

On attempting to prepare a benzoyl derivative of the β -hydrazone, the principal product was found to consist of the substance just described, but the residue from the mother liquor remained oily during many months, suggesting that both isomerides are formed. The α -benzoyl derivative was obtained also by mixing equal quantities of camphorquinone and benzoylhydrazine in dilute alcohol, crystals separating after two hours at 40° ; in this case, also, the filtrate deposited an oil, indicating the presence of a mixture.

Benzylidene Derivative of Camphorquinonehydrazone,



The α -hydrazone was finely powdered, mixed with the calculated amount of benzaldehyde, and heated with a few c.c. of alcohol during two or three minutes; crystals did not separate on cooling, but water precipitated a yellow oil, which quickly became solid, and was recrystallised from boiling petroleum (b. p. 60 – 80°). The massive, yellow crystals melted at 109.5° :

0.1253 gave 12.0 c.c. N_2 at 20.5° and 758 mm. $\text{N} = 10.90$.

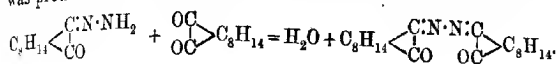
$\text{C}_{17}\text{H}_{26}\text{ON}_2$ requires $\text{N} = 10.44$ per cent.

The substance is freely soluble in chloroform, benzene, acetone, alcohol, and ethyl acetate, but only moderately so in warm petroleum; a solution containing 0.3035 gram, made up to 20 c.c. with chloroform, gave α_D $4^\circ 50'$ in a 2-dcm. tube, whence $[\alpha]_D$ 159.2° . It is also produced immediately on shaking the finely powdered hydrazone with water and benzaldehyde, but the method is not convenient, as a portion of the hydrazone remains mechanically protected.

The same benzylidene derivative is produced on agitating the β -hydrazone suspended in water with the aldehyde, the deep yellow colour of the condensation product becoming noticeable immediately. Owing to the solubility of the β -hydrazone in water, none escapes combination, but the product remains liquid during many days, although rapidly becoming solid when heated to 100° and scratched.

Another example of the capacity of the hydrazones for taking part in condensation changes was given by heating an alcoholic solution of the α -hydrazone and camphorquinone in molecular pro-

portion during twelve hours under reflux, when azocamphanone was produced:



Oxidation of the Hydrazones to Diazocamphor.

Since it was desirable to study the oxidation of the hydrazones under conditions precluding the likelihood of preliminary inter-conversion, it occurred to us that mercury acetamide, owing to its solubility in cold water, might be a more suitable agent than mercuric oxide, a study of the acetamide compound having shown that it acts rapidly on primary hydrazines with precipitation of mercury (Trans., 1898, 73, 783). Experiment showed that the behaviour of the isomeric hydrazones of camphorquinone towards this agent distinguishes itself sharply from the indifference of azocamphanone. It having been first ascertained that the β -hydrazone is not transformed into the isomeride by dissolution in pyridine, 1 gram dissolved in 3 c.c. of the cold solvent was treated with 2 grams of mercury acetamide in 3 c.c. of cold water, the metal being precipitated immediately. The production of the diazo-compound was indicated on extracting with ether, which became deep yellow, and, after evaporation, the pyridine residue yielded 0.8 gram of diazocamphor on dilution with water; recrystallisation from petroleum (b. p. 40°) gave long, striated, yellow prisms, melting at 73–74°.

Procedure in the case of the α hydrazone was modified by the sparing solubility of the substance, 5 grams of which were dissolved in 80 c.c. of hot pyridine, cooled to 50–60°, and treated with 10 grams of mercury acetamide in 30 c.c. of warm water; mercury was precipitated immediately, and 4 grams of diazocamphor obtained. A solution containing 0.4605 gram of the diazo-compound, made up to 25 c.c. with chloroform, gave $\alpha_D 4.058'$ in a 2-dm. tube, whence $[\alpha]_D 134.8^\circ$.

Reduction of Diazocamphor to the Hydrazones.

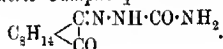
A 20 per cent. solution of diazocamphor in absolute alcohol was saturated with hydrogen sulphide without undergoing any change in appearance, but on adding a few drops of dilute ammonia and again passing the gas, the liquid became pale brown, and gradual separation of the α -hydrazone took place; on subjecting the filtrate to steam distillation, a small proportion of the β -hydrazone was carried over. As it is a matter of importance to establish the production of both compounds without question, the experiment

was repeated at zero, when it was found that the precipitation of the α -hydrazone was diminished, and the yield of β -hydrazone was proportionately increased.

Reduction of the α -Hydrazone to α -Aminocamphor.

Owing to the readiness with which the hydrazones undergo acetylation, a certain amount of the α -acetyl derivative is formed on attempting to reduce the α -hydrazone with zinc dust and acetic acid; it is precipitated, however, when the acid is neutralised. On adding a further quantity of alkali to the filtrate, ammonia is set free, and ether extracts aminocamphor, which may be identified by conversion into the oxime; a specimen of aminocamphoroxime obtained in this way melted at 144–145°.

The Isomeric Camphorquinonesemicarbazones,



The discovery of a second camphorquinonesemicarbazone arose from the observation that on evaporating the filtrate from the substance described by Lapworth and Chapman, there is deposited an oil which, by treatment with very dilute aqueous alkali, is divisible into two solids; one passes into solution, and consists of the derivative already known, whilst the new semicarbazone remains suspended.

A solution containing 33.2 grams of camphorquinone in 150 c.c. of alcohol was mixed with semicarbazide acetate prepared from 22.2 grams of the hydrochloride and 27 grams of crystallised sodium acetate in 100 c.c. of water; the liquid, from which crystals of the α -semicarbazone quickly separated, was transferred to a stoppered filtering flask connected with a water-pump, the alcohol being evaporated at the laboratory temperature during six to eight hours, when drops of oil became noticeable among the crystals. From the resulting sludge about 16 grams of the less soluble α -semicarbazone were filtered, the mother liquor being poured into water and treated with alkali hydroxide until a faint yellow colour persisted; the suspended oil became solid when stirred, and consisted of the more soluble β -semicarbazone mixed with a small proportion of the isomeride. In order to remove the latter, the filtered product was ground three or four times with 10 c.c. of 2 per cent. aqueous sodium hydroxide, the filtration necessary after each extraction being carried out as quickly as possible, because although the α -semicarbazone dissolves in weak alkali without delay, the β -modification is also soluble, but very slowly. The pale yellow powder was then extracted twice with 300 c.c. of boiling water, the

crystalline deposit (6 grams) from this being recrystallised from 25 c.c. of warm benzene, to which the same volume of petroleum was added. At this stage the purification was complicated by the fact that following closely on the slender, yellow crystals of the β -semicarbazone there appeared opaque nodules containing the isomeride.

Camphorquinone- α -semicarbazone is the substance described by Lapworth and Chapman (*loc. cit.*). It crystallises from alcohol in lustrous, colourless prisms, melting and evolving gas at 236° , after sintering and becoming yellow at about 230° ; it is much less readily soluble in organic media than the isomeride, and is insoluble in petroleum. A solution containing 0.3152 gram, made up to 20 c.c. with methyl alcohol, gave α_D $8^{\circ}45'$ in a 2-dm. tube, whence $[\alpha]_D$ 277.6° . As distinguished from the β -compound, it dissolves immediately in dilute alkali, and 0.3344 gram in sufficient potassium hydroxide, made up to 25 c.c. with water, gave α_D $8^{\circ}55'$ in a 2-dm. tube, whence $[\alpha]_D$ 233.3° ; this remained constant during six days, and the semicarbazone precipitated from the solution by acetic acid was unchanged material. Nevertheless, on heating with 10 per cent. potassium hydroxide during three to four days, camphor was gradually produced. Cold concentrated sulphuric acid dissolves the α -semicarbazone, and gradually changes it to azocamphanone, which is precipitated on pouring the liquid into water; if, however, the hot acid is used, a certain amount of camphorquinone is produced. An estimation of the molecular weight in boiling chloroform gave 236 instead of 223.

Camphorquinone- β -semicarbazone crystallises in pale yellow prisms, melts at 147° , and is readily soluble in alcohol, acetone, ethyl acetate, chloroform, ether, or benzene, but dissolves only sparingly in hot water or boiling petroleum: *

0.2328 gave 0.5037 CO_2 and 0.1539 H_2O . $\text{C} = 59.03$; $\text{H} = 7.66$.

0.3225 „ 54.8 c.c. N_2 at 25° and 754 mm. $\text{N} = 18.79$.

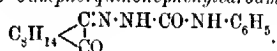
$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$ requires $\text{C} = 59.19$; $\text{H} = 7.62$; $\text{N} = 18.83$ per cent.

A solution containing 0.3152 gram, made up to 20 c.c. with methyl alcohol, gave α_D $6^{\circ}20'$ in a 2-dm. tube, whence $[\alpha]_D$ 200.9° . When covered with aqueous alkali hydroxide, the β -semicarbazone does not appear to dissolve; if, however, the solid substance is thrown into hot 10 per cent. sodium hydroxide, there is produced immediately a deep yellow solution, the colour of which gradually fades, owing to the formation of the oxytriazine (see below). On raising the temperature of the fused β -semicarbazone to about 190° , the substance became solid, and the α -semicarbazone was found to have been produced.

Conversion of the Semicarbazones into the Acetylhydrazones.

The semicarbazones were separately heated with boiling acetic anhydride during one hour, the solid product obtained in each case, on pouring the liquid into water, being found to consist of a mixture of the α - and β -acetyl derivatives of the hydrazones. The transformation was not easy to establish experimentally, because the relative solubility of the acetyl derivatives in alkali exactly resembles that of the semicarbazones themselves, and as the melting points of the latter differ from those of the respective acetyl hydrazones by 3° only in each case, the preliminary experiments led to the supposition that the semicarbazones are directly interconvertible by the action of the agent in question.

The Isomeric Camphorquinonephenylcarbamylhydrazones,



These derivatives were prepared by three different methods.

(1) Action of hot aniline on the α - and β -semicarbazones, each of which gave both phenylcarbamylhydrazones.

(2) Condensation of camphorquinone with phenylcarbamylhydrazide, also yielding a mixture.

(3) Interaction of phenylcarbimide and the α - and β -hydrazones, which led to the individual phenylcarbamylhydrazones, respectively.

Camphorquinone- α -phenylcarbamylhydrazone.—Four grams of the α -semicarbazone were dissolved in 20 c.c. of aniline, and heated ten minutes at the boiling point of the solvent, ammonia being liberated freely before this temperature was reached; the cooled liquid was diluted with its volume of alcohol, and poured into 200 c.c. of 10 per cent. acetic acid at zero. The precipitated oil quickly hardened when scratched, and on dissolving the product in 80 c.c. of hot methyl alcohol, the α -phenylcarbamylhydrazone crystallised in thick, colourless plates, melting at 211°, whilst the isomeride remained dissolved:

0.2494 gave 0.6096 CO_2 and 0.1656 H_2O . $\text{C}=66.67$; $\text{H}=7.43$.

0.1660 „ 20.3 c.c. N_2 at 24° and 761.5 mm. $\text{N}=13.75$.

$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}_3\frac{1}{2}\text{CH}_4\text{O}$ requires $\text{C}=66.64$; $\text{H}=7.30$; $\text{N}=13.33$ per cent.

The transparent crystals became opaque in the steam-oven, owing to loss of crystal-alcohol:

0.2462 gave 0.6158 CO_2 and 0.1546 H_2O . $\text{C}=68.23$; $\text{H}=7.03$.

$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}_3$ requires $\text{C}=68.23$; $\text{H}=7.03$ per cent.

Ordinary solvents, excepting petroleum, dissolve the substance readily, but, unlike the α -semicarbazone, it is insoluble in cold

aqueous alkali hydroxide, although dissolving when heated, with development of a yellow coloration. A solution containing 0.2207 gram, made up to 25 c.c. with chloroform, gave α_D $4^{\circ}3'$ in a 2-dcm. tube, whence $[\alpha]_D$ 229.3° . An estimation of the molecular weight by depression of the melting point of benzene gave 327 instead of 299.

Camphorquinone- β -phenylcarbamyldiazone.—From the mother liquor of the foregoing substance there gradually separated long, slender, silky needles, in which a few small crystals of the α -compound were embedded, and as the latter remained undissolved on rapidly warming the liquid, it was possible to isolate the β -modification without much difficulty, the final recrystallisation being effected by adding petroleum to a solution of the needles in benzene. The substance is very pale yellow, and melts at 161° :

0.2142 gave 0.5346 CO_2 and 0.1372 H_2O . $\text{C}=68.10$; $\text{H}=7.17$.

0.1062 „ 13.9 c.c. N_2 at 24° and 754 mm. $\text{N}=14.55$.

$\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_3$ requires $\text{C}=68.23$; $\text{H}=7.03$; $\text{N}=14.09$ per cent.

In all common media the solubility of the β -phenylcarbamyldiazone scarcely differs from that of the isomeride, but the tendency to form supersaturated solutions is much greater. A solution containing 0.2128 gram, made up to 25 c.c. with chloroform, gave α_D $3^{\circ}16'$ in the 2-dcm. tube, whence $[\alpha]_D$ 191.9° .

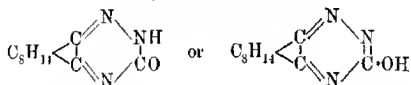
As in the case of the β -semicarbazone, transformation into the α -modification was readily accomplished by heating the β -phenylcarbamyldiazone above its melting point; the clear liquid which had been carried to 200° remained vitreous on cooling, but immediately became crystalline on being scratched in presence of a small quantity of methyl alcohol.

In preparing the phenylcarbamyldiazones by the foregoing method, it was noticed that the proportion of the two modifications depends on the duration of heating and on the temperature reached. This is explained by the fact that either is convertible into the other isomeride by the action of hot aniline, each individual yielding an equilibrium mixture when a solution in that base is heated until the solvent boils; roughly speaking, the relation between the constituents of this mixture is $\alpha:\beta=2:1$.

The second process for obtaining the phenylcarbamyldiazones was practised by mixing solutions containing 5 grams of camphorquinone and 4.5 grams of phenylcarbamyldiazide, $\text{C}_6\text{H}_5\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, each in 15 c.c. of hot methyl alcohol, and heating the liquid on the water-bath during a few minutes; 2.8 grams of the α -phenylcarbamyldiazone separated on cooling, whilst the mother liquor deposited a mixture of this with the characteristic, silky needles of the β -modification.

The third method is the most convenient when the hydrazones are available, because it leads to the individuals, and thus obviates the necessity of a tedious separation. The finely powdered α -hydrazone (1.8 gram), suspended in 250 c.c. of boiling benzene, in which it was not completely soluble, was heated with 3 grams of phenylcarbimide on the water-bath during two hours, when the liquid did not deposit crystals on cooling. After distilling off the solvent until only 30 c.c. remained, twice this volume of petroleum was added, precipitating 2.7 grams of a crystalline powder, readily identified with the α -phenylcarbamyldhydrazone on recrystallisation. In preparing the β -modification by this process, 0.9 gram of the β -hydrazone, dissolved in 10 c.c. of benzene, was treated with 0.7 gram of phenylcarbimide, the mixture being left at the laboratory temperature, and after the lapse of twelve hours diluted with petroleum until pale yellow needles appeared; after recrystallisation it melted at 161° , and did not depress the melting point of the β -phenylcarbamyldhydrazone prepared by the other methods.

Camphane-orytriazine,



Whilst the α -semicarbazone is dissolved immediately by aqueous alkali hydroxide, forming a permanent yellow solution, the β -modification is transformed into the anhydride represented above, the conversion taking place at rates depending on the temperature.

Camphorquinone- β -semicarbazone was covered with 10 parts of 10 per cent. aqueous sodium hydroxide, and shaken at intervals during five hours, when the solid substance, at first coloured yellow by the agent, had passed into a colourless solution. After extraction with ether, dilute sulphuric acid was added until the initial precipitate was redissolved, when the liquid was shaken eight times with ether; the solvent deposited 85 per cent. of viscous residue, which quickly solidified. Recrystallisation from warm benzene, to which petroleum was added, gave colourless, transparent pyramids, melting at 166 – 167° :

0.2183 gave 0.5137 CO_2 and 0.1406 H_2O . $\text{C}=64.18$; $\text{H}=7.21$.

0.1950 „ 35.6 c.c. N_2 at 21° and 759 mm. $\text{N}=20.75$.

$\text{C}_{11}\text{H}_{15}\text{ON}_3$ requires $\text{C}=64.39$; $\text{H}=7.31$; $\text{N}=20.49$ per cent.

The substance is somewhat readily soluble in warm water, and does not crystallise completely on cooling; alcohol, ether, chloroform and benzene dissolve it readily, but it is insoluble in petroleum. It

does not reduce Fehling's solution, and when heated with ammoniacal silver oxide yields a voluminous, white precipitate, freely soluble in ammonia. A solution in sodium carbonate is strongly alkaline, and gives a transient violet precipitate with ferrous sulphate, becoming bright green when excess is added; copper salts produce an apple-green precipitate, also formed by nickel sulphate, excess of which yields a clear solution. The optical activity of the oxytriazine and its derivatives is very much lower than that of the foregoing compounds of camphorquinone; a solution containing 0.2855 gram, made up to 25 c.c. with chloroform, gave α_D 0.31' in a 2-dcm. tube, whence $[\alpha]_D$ 22.6°.

The *acetyl* derivative was readily formed on heating the oxytriazine with acetic anhydride; after recrystallisation from a mixture of benzene and petroleum, it melted at 168—169°:

0.1765 gave 0.4096 CO₂ and 0.1127 H₂O. C=63.30; H=7.14.

C₁₃H₁₇O₂N₃ requires C=63.16; H=6.88 per cent.

The substance dissolves freely in cold benzene, chloroform, acetone, or methyl alcohol, but is less readily soluble in ethyl alcohol or ethyl acetate, from which it crystallises in lustrous, colourless needles. A solution containing 0.2444 gram, made up to 20 c.c. with chloroform, gave α_D 1.2' in a 2-dcm. tube, whence $[\alpha]_D$ 42.2°.

The *benzoyl* derivative, prepared by the action of benzoyl chloride in pyridine solution and purified by precipitation from acetic acid, followed by recrystallisation from a mixture of benzene and petroleum, melted at 193—194°:

0.2021 gave 0.5150 CO₂ and 0.1108 H₂O. C=69.51; H=6.13.

C₁₅H₁₉O₂N₃ requires C=69.90; H=6.15 per cent.

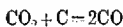
The compound is freely soluble in cold acetone or chloroform, but ethyl acetate, methyl alcohol, benzene, or ethyl alcohol dissolve it less readily, and it is very sparingly soluble in boiling petroleum. A solution containing 0.2808 gram, made up to 20 c.c. with chloroform, gave only α_D 0.13' in a 2-dcm. tube, whence $[\alpha]_D$ 7.7°.

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CCXXVI.—*The Effect of Temperature on the
Equilibrium $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

THE fact that carbon monoxide dissociates under the influence of heat, yielding carbon dioxide and carbon, or, in other words, the fact that the reaction:

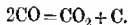


is reversible, was discovered by H. Sainte-Claire Deville in 1864 (*Compt. rend.*, 1864, 59, 873; 1865, 60, 317) by means of his "hot-cold" tube. He was able to observe only a small degree of dissociation at a temperature a little lower than the melting point of silver, whilst at temperatures above 1000° none at all could be detected.

Since it was assumed that the degree of dissociation of carbon monoxide, like that of carbon dioxide and steam, should increase with increased temperature, doubt was cast on Deville's first experiments, and it was suggested that the formation of carbon dioxide and the deposition of carbon were due to the chemical action of the glaze of the porcelain tubes he employed.

In 1869 Sir Lothian Bell (*Journ. Chem. Soc.*, 22, 203), while studying the reactions taking place in the blast-furnace, found that such portions of the iron ore as had been subjected to the action of carbon monoxide at comparatively low temperatures in the upper part of the furnace were impregnated with carbon, presumably arising from the dissociation of the gas. He thereupon instituted laboratory experiments to determine the action of carbon monoxide on different oxides at different temperatures.

As a result of these experiments, Bell was able to state that the reduced metal was as effective as the oxide in determining the decomposition of carbon monoxide, and he gave the equation of the reaction as being:



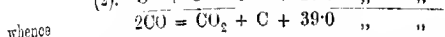
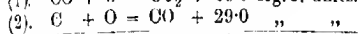
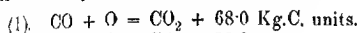
He also showed that the oxides of nickel and cobalt and the reduced metals acted in a similar manner to iron oxide and reduced iron.

The influence of temperature on the amount of decomposition in a given time was also studied by Bell, comparative figures being obtained from the quantities of carbon deposited. This is well shown in the following series of experiments, in which carbon

monoxide was passed slowly over reduced iron at different temperatures during six hours:

| | | | | | |
|---|------|------|------|------|------|
| Temperature | 250° | 400° | 500° | 600° | 800° |
| Carbon deposited. (Grams per 100 grams of iron) | 4.7 | 181 | 95 | 6 | 0.3 |

It is thus apparent that a low temperature favours the decomposition, a result which explains the failure of Deville and others to obtain evidence of dissociation at 1000°, and is in accordance with the fact that the reaction $2\text{CO} = \text{CO}_2 + \text{C}$ is exothermic. The heat of reaction is shown by the following equations:



Since the reaction is reversible, an equilibrium must be established between the quantities of carbon dioxide and monoxide that can exist together in the presence of carbon; and, in accordance with van't Hoff's principle of mobile equilibrium, the quantity of carbon monoxide will be increased by lowering the temperature.

The equilibrium at different temperatures has been studied by O. Boudouard (*Ann. Chim. Phys.*, 1901, [vii], **24**, 5), who has given figures for 650°, 800°, and 925°.

In studying the reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$, Boudouard made use of iron, nickel, and cobalt as catalysts. The finely divided metals were obtained by impregnating broken pumice with the nitrates and igniting, the oxides thus formed being afterwards heated in a stream of carbon monoxide until reduction was considered to be complete.

For the experiments at temperatures below 700°, glass tubes, 6 to 7 cm. long and 1.5 cm. in diameter, were used, the total volume of gas being from 12 to 15 c.c. Above 700°, a porcelain tube, 40 cm. long and of 2.4 cm. internal diameter, was employed, the pumice containing the catalyst occupying the middle 10 cm. of the tube, and the remainder being packed with broken porcelain.

The main results were as follow:

| Temperature, | Catalyst. | Duration of heating, | Carbon dioxide, per cent. |
|--------------|-----------|----------------------|------------------------------|
| 445° | iron | 6 hours | 100 |
| 445 | nickel | 1 hour | 100 |
| 445 | cobalt | 1 " | 100 |
| 650 | cobalt | 7 " | 61 |
| 800 | nickel | 4 " | 6.7 |
| 800 | cobalt | 4 " | 6.5 |

In one experiment at 445°, using a very small quantity of iron oxide (reduced by carbon monoxide) as catalyst, Boudouard obtained 52.3 per cent. of carbon dioxide and 47.7 per cent. of carbon monoxide remaining after six hours' heating.

The reverse reaction, $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$, was studied in a similar manner, but without the use of catalysts, purified wood charcoal being employed. The carbon was heated in an atmosphere of carbon dioxide in tubes sealed at one end, with the other end open and bent so as to dip under mercury, the object being to avoid bursting of the tubes due to increased pressure as the reaction proceeded.

The results were as follow:

| Temperature. | Duration of heating, hours. | Carbon dioxide, per cent. |
|--------------|--------------------------------|------------------------------|
| 650° | 9 | 62.4 |
| 650 | 12 | 61.5 |
| 800 | 6 | 6.7 |
| 800 | 6 | 6.8 |

In addition to the above, two experiments were made at 925°, in which a measured volume of carbon dioxide was passed in a slow stream through the heated charcoal, and the resulting gases bubbled through baryta water, the barium carbonate that was precipitated being afterwards weighed. Assuming that a single passage of the carbon dioxide over the heated charcoal was sufficient to establish equilibrium, Boudouard calculated from one experiment 3.3 per cent., and from the other 4.5 per cent., of carbon dioxide remaining in equilibrium with carbon monoxide over carbon at 925°.

Boudouard's experiments prove that the equilibrium ratio CO/CO_2 in contact with carbon is a function of temperature, and the results are in general agreement with the laws respecting equilibria in gaseous systems.

R. Schenck and F. Zimmermann (*Ber.*, 1903, 36, 1), while studying more particularly the order of the reactions taking place, have been able to prove that the oxides of iron, nickel, and cobalt are quite ineffective in determining the dissociation of carbon monoxide, and that it is only the reduced metals that act catalytically. This is in direct opposition to the views advanced by Boudouard. At the same time Schenck and Zimmermann give results for the equilibrium at low temperatures (445° and 508°) that are entirely at variance with those of Boudouard. At 445° Boudouard regards the dissociation of carbon monoxide as complete; while Schenck and Zimmermann, using reduced iron as catalyst, obtained 52.8 per cent. of carbon monoxide as the quantity remaining in equilibrium at that temperature. It is interesting to note that this figure agrees fairly well with that obtained by Boudouard when using only a small quantity of iron as catalyst (a result which he discards), and it seems probable that in those experiments, otherwise inexplicable, in which he obtained complete decomposition of carbon monoxide, the oxides of the metals used as catalysts were incom-

pletely reduced before the tubes were sealed, and that oxidation of the carbon monoxide took place.

We considered it desirable to determine the equilibrium ratio more accurately and for a greater number of temperatures, avoiding the use of catalysts, for Boudouard's method of experiment did not appear to us to be calculated to give very accurate results, and his figures were not in agreement with those obtained by us during the course of an investigation on the mode of burning of carbon on which we are still engaged.

The method we have adopted has been to circulate carbon dioxide continuously over purified wood charcoal packed in a porcelain tube, and heated in an electric resistance furnace.

We have obtained in this manner the following figures for the percentages of carbon dioxide and monoxide that are in equilibrium in the presence of excess of carbon at different temperatures:

| Temperature. | Carbon dioxide. | Carbon monoxide. |
|--------------|----------------------|------------------|
| | Per cent. by volume. | |
| 850° | 6.23 | 93.77 |
| 900 | 2.22 | 97.78 |
| 950 | 1.32 | 98.68 |
| 1000 | 0.59 | 99.41 |
| 1050 | 0.37 | 99.63 |
| 1100 | 0.15 | 99.85 |
| 1200 | 0.06 | 99.94 |

The percentages are calculated as those of the nitrogen-free gases. The gases usually contained from 1 to 2 per cent. of nitrogen.

In Le Chatelier's general formula for equilibrium in gaseous systems:

$$500 \int \frac{dT}{T^2} + (N'' - N') \log_e P + \log_e \frac{c_1^{n_1} c_2^{n_2} \dots}{c_3^{n_3} c_4^{n_4} \dots} = k$$

L = the total heat of the reaction at absolute temperature T .

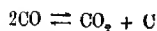
P = the pressure in atmospheres.

N and N' = the number of molecules on the left- and on the right-hand side of the equation.

n_1, n'_1, \dots and n_2, n'_2, \dots = the number of molecules of the different substances taking part in the reaction, index 1 meaning the initial and index 2 the final system.

c_1, c'_1, \dots and c_2, c'_2, \dots = the concentrations of the different substances, indices as above.

In the system:



$n_1 = 2; n_2 = 1; n'_1 = 0; c'_2 = 0$.

If the system is in equilibrium at atmospheric pressure, $P = 1$, and the expression

$$(N'' - N') \log_e P = 0.$$

Assuming with Le Chatelier that the heat of reaction is constant, and introducing its value (39.0 Kg.C. units), the equation then becomes:

$$\frac{19,500}{T} + \log_e \frac{c_1^2}{c_2} = k.$$

The values for k calculated from our results are as follow:

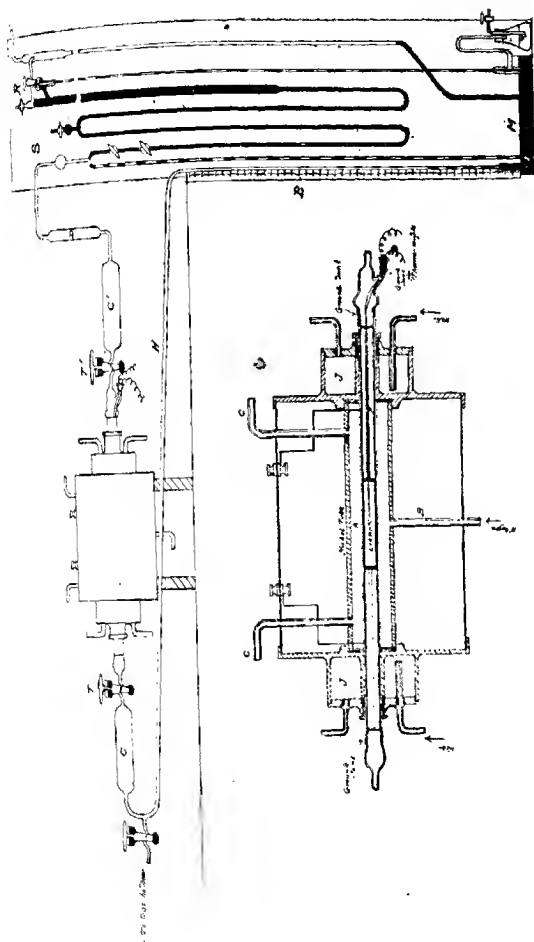
| T . | c_1 . | c_2 . | k . |
|-------|---------|---------|-------|
| 1123° | 0.9377 | 0.0623 | 20.01 |
| 1173 | 0.9773 | 0.0222 | 20.39 |
| 1223 | 0.9863 | 0.0132 | 20.21 |
| 1273 | 0.9941 | 0.0059 | 20.41 |
| 1323 | 0.9963 | 0.0037 | 20.32 |
| 1373 | 0.9985 | 0.0015 | 20.70 |
| 1473 | 0.9994 | 0.0006 | 20.65 |

EXPERIMENTAL.

The Equilibrium Furnace.—In designing the equilibrium furnace, the two chief considerations were (a) the obtaining of a uniform temperature, and (b) the attainment of rapid cooling of the gases after they had left the zone of reaction, in order to "fix" the equilibrium. We had, moreover, to recognise the fact that at temperatures above 1000° both porcelain and fused silica or quartz tubes, such as we intended to employ for the reaction vessel, become slightly porous to gases.

The construction of the furnace, which was made for us by Messrs. C. W. Cook and Co., at the University Engineering Works, Manchester, is shown in Fig. 1. It consists essentially of a glazed Berlin porcelain tube, 51 cm. long and of 28 mm. external and 20 mm. internal diameter, wound with platinum wire, through which an electric current can be passed. The winding is arranged so as to give a uniform temperature throughout the central portion of 12 cm., and is carried on either side close up to the gunmetal water-jackets, J , being insulated from them by thin disks of porcelain. By winding the coils closer near each end than along the rest of the tube, we are able, when a fairly rapid stream of water is passing through the jackets, to obtain a sudden reduction in the temperature of the tube from 1000° in the central uniform portion to 400° or less within a distance of 1.5 cm.; while the temperature falls to below 150° within a distance of 5 cm.

This result is not attained solely as the effect of water-cooling and increasing the length of resistance wire at the ends, but is in part due to the double-jacketing arrangement, A , which is intended primarily to avoid any error due to porosity of the porcelain tube at high temperatures. A nickel tube, 22 cm. long and of 7.1 cm. external and 5.7 cm. internal diameter, is fixed coaxially with the



porcelain tube, and through the annular space a slow stream of dry nitrogen is passed. The nitrogen, prepared by Harcourt's method, enters under a slight pressure through the central tube *B*, and issues at *C, C* through wash-bottles containing concentrated sulphuric acid. The passing of this stream of dry nitrogen, in addition to ensuring that no oxygen or water vapour enters the porcelain tube if it becomes porous at high temperatures, causes a more uniform distribution of heat throughout the length of the furnace, an effect which is enhanced by the position of entrance of the gas.

The furnace tubes are surrounded by a thick layer of kieselguhr to prevent loss of heat by radiation, and the whole is encased in a jacket of sheet iron.

The carbon used throughout this research has been wood charcoal purified by first digesting with concentrated hydrochloric acid (in a bolt-head flask fitted with a reflex condenser) to remove the ash; washing with distilled water; and subsequently heating at 1000° in a stream of dry chlorine, washing, heating in a stream of hydrogen, and finally in a vacuum at 1000° for forty-eight hours. It is crushed and sieved so as to pass through a 10-mesh sieve and remain on a 20-mesh, and about 6 grams are then loosely packed into a thin tube of quartz, 12 cm. long and open at both ends, which slides easily into the porcelain tube.

After the insertion of the quartz sheath containing the carbon, a plug of silica, 16.5 cm. long and 1.9 cm. in diameter with a hole 3 mm. in diameter drilled through the centre, is introduced at each end. These plugs serve to keep the carbon surface in position in the zone of constant temperature, but they are intended more especially to cause the stream of gases, after passing over the heated carbon, to pass rapidly out of the tube, and thus ensure that the equilibrium determined shall be that of the experimental temperature recorded.

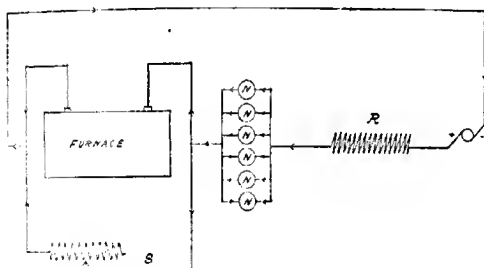
The Measurement of Temperature.—The temperatures are measured by means of a platinum and platinum-rhodium thermocouple, and recorded by one of the Cambridge Scientific Instrument Company's "Thread-Recorders." The couple is embedded in the middle of the carbon, the leads being insulated by thin quill tubing of quartz, and the whole enclosed in a sheath of thin quartz, which passes easily through the bore of the plug *P*.

Some little difficulty was at first experienced in maintaining a constant temperature, owing to fluctuations in the voltage of the electric current supplied to the furnace. Since the experiments extended continuously over several days, or, in some cases, several weeks, personal attention was found to be impossible, and a means

had to be devised of automatically regulating the voltage. The method finally employed, for the suggestion of which we are indebted to Mr. E. Muller, of the Cambridge Scientific Instrument Company, is as follows.

The voltage of the main current is first cut down by the large resistance, R (Fig. 2), to within a small margin of that required to obtain the experimental temperature in the furnace. It then passes through the Nernst lamp steadying resistances, N , of which a sufficient number are arranged in parallel to allow the requisite quantity of current to pass round the circuit. These steadying resistances take as their normal current 1 ampere at 15 volts, whilst the furnace, when hot, takes about 3 amperes. The exact number that are required to ensure perfect regulation and automatic adjustment of the voltage across the furnace terminals depends on the experimental temperature employed; there must be a sufficient

FIG. 2.



number to ensure that the spirals of fine iron wire within the exhausted globes of each shall glow a dull red without becoming overheated; for they depend for their action on the change in electrical resistance that occurs in iron wire at a temperature of about 775° .

After passing through the Nernst lamp resistances, the current is divided, part going through the furnace, and part through the shunt, S , containing a rheostat. About equal quantities of current pass through the furnace and the shunt. The final adjustment of the voltage across the furnace to that required to obtain a given temperature is made by means of the rheostat in the shunt, the alteration of which does not interfere with the main current, since the whole of it passes through the Nernst lamp resistances.*

This method has proved eminently satisfactory, the experimental temperature being maintained without any serious fluctuations continuously during several weeks.

General Arrangement of Apparatus.—The reacting gases are circulated without interruption over the heated carbon until equilibrium is attained. The general form of the circulation apparatus is that designed by one of us in conjunction with W. A. Bone for the investigation of the slow combustion of hydrocarbons (Trans., 1903, 83, 1074).

The porcelain tube containing the carbon carries a ground glass joint at each end held firmly in position by strong springs. These joints make connexion on either side, through the mercury-cup taps *T*, *T'* (Fig. 1), with the cylindrical vessels *C*, *C'*, each of 200 c.c. capacity. These vessels mainly determine the capacity of the apparatus, and are cylindrical in form in order to allow of being heated to drive off any traces of gas that may have a tendency to stick to the glass.

On the right-hand side, connexion is made, through the calcium chloride drying-tube *D*, to the head of the Sprengel pump *S*. On the left is fused a long tube of wide bore, which passes horizontally across the front of the furnace and is then bent downwards at right angles, forming a manometric tube, which stands over the delivery-tube of the Sprengel pump in the mercury trough *M*. A short T-piece near the left hand cylinder, closed by a mercury-cup tap, serves for the introduction of the gas.

With the exception of the ground joint connexions to the porcelain tube, the apparatus is of fused glass throughout.

The gases are drawn, by means of the automatic Sprengel pump, through the furnace, and delivered under mercury in the trough *M* into the manometric tube *B*, whence they return along the horizontal tube *H* to the cylinder *C*, and are again drawn forward through the furnace. The automatic Sprengel pump, the general construction of which is described in the paper referred to above (*loc. cit.*, p. 1079), is actuated by suction produced by a double-acting Geryk pump driven by an electric motor, and is so arranged that the head of mercury in the reservoir *R* allows of the gases being circulated at atmospheric pressure.

The total volume of the apparatus, measured at 0°, is 570 c.c.; that of the packed porcelain tube 96 c.c.

The Gas Analyses.—The carbon dioxide was prepared by dropping boiled concentrated sulphuric acid from a separating funnel into a boiled solution of sodium carbonate contained in an Erlenmeyer flask. The gas evolved was passed through two sulphuric acid worms, and collected in a glass gas-holder containing concentrated sulphuric acid, over which it was stored for two weeks before being used for an experiment.

The carbon monoxide was prepared from sodium formate, made

into a stiff paste with distilled water, by the action of concentrated sulphuric acid. It was washed through two worms containing potassium hydroxide solution, and stored over sulphuric acid in the same manner as the carbon dioxide.

The gases remaining after an experiment were analysed volumetrically in a Bone and Wheeler gas analysis apparatus over mercury, from 200 to 300 measures of gas being taken for an analysis. Carbon dioxide was estimated by absorption with as small a quantity of aqueous potassium hydroxide as possible, or when only small quantities were present, by absorption with a concentrated solution of barium hydroxide. Carbon monoxide was absorbed by an ammoniacal solution of cuprous chloride, prepared by passing ammonia gas into distilled water containing the freshly precipitated cuprous chloride in suspension until the latter was dissolved. A little ammonium chloride was added to the solution as thus prepared to reduce the tension of ammonia vapour. The gas was treated twice with small quantities of this solution, and afterwards washed with dilute sulphuric acid.

Any residue (which never amounted to more than 2 per cent. of the total gas) was afterwards exploded with a measured volume of air and oxygen, to which a few c.c. of pure electrolytic gas were added. Any contraction in volume after explosion, or after absorption with potassium hydroxide, was then determined. A trace of hydrogen due to insufficient drying of the gases, or to moisture in the circulation apparatus, was detected in several experiments the results of which were discarded.

Method of Conducting an Experiment.—The apparatus having been thoroughly exhausted, the glass being heated in a large blow-pipe flame to drive off the last traces of air, the carbon dioxide (or monoxide) is introduced in such quantity that when the reaction is complete the gases shall be as nearly as possible at atmospheric pressure. As a preliminary to a series of experiments, a certain quantity of carbon dioxide is introduced to the carbon heated to 1000° and allowed to circulate for several days. The resulting gases are then pumped out, and the furnace brought to the experimental temperature. This preliminary treatment serves to remove any traces of water-vapour that still remain in the apparatus; it was in the gases resulting from such experiments that we were able to detect traces of hydrogen.

In the experiments proper the gases are allowed to circulate for twenty-four hours after the volume, as indicated by a scale fixed behind the manometric tube, has ceased to change. The reaction tube is then shut off from the rest of the apparatus, and samples are withdrawn for analysis.

Results of Experiments.

The results of our experiments can best be expressed in tabular form as follow:

| Experiment number. | Temperature. | Duration of heating, hours. | Composition of resulting gases (calculated as nitrogen-free mixture). | |
|--------------------|--------------|-----------------------------|---|-------|
| | | | CO ₂ . | CO. |
| E 14 | 850° | 240 | 6.23 | 93.77 |
| E 9 | 900 | 180 | 2.22 | 97.78 |
| E 16 | 950 | 144 | 1.32 | 98.68 |
| E 4 | 1000 | 48 | 0.59 | 99.41 |
| E 18 | 1050 | 48 | 0.37 | 99.62 |
| E 5 | 1100 | 48 | 0.15 | 99.85 |
| E 6 | 1200 | 48 | 0.06 | 99.94 |

In addition, we have made two attempts to attain equilibrium at a temperature of 800° with the circulation apparatus, but have abandoned the experiments after they had continued for six weeks without showing signs of coming to a conclusion, 20 per cent. of carbon dioxide still remaining after that time.

Boudouard, in the reduction of carbon dioxide by wood charcoal without the presence of a catalyst, states that equilibrium was attained in his experiments after six hours' heating at 800° and after twelve hours' heating at 650°, the percentages of carbon dioxide remaining in equilibrium being 6.3 and 61.5 per cent. respectively at the two temperatures. The volume of his apparatus was only from 12 to 15 c.c. as against our 570 c.c., but we do not think that this fact is sufficient to explain the marked discrepancy between our results, since we used a correspondingly larger quantity of carbon surface. In another series of experiments that we are making on the rate of reduction of carbon dioxide by wood charcoal at different temperatures, we have been unable to obtain a disappearance of carbon dioxide of more than 0.7 per cent. after 122 hours' heating at 700°.

All our experiments recorded above have been made starting with an initial concentration of 100 per cent. carbon dioxide; for the rate at which the reverse reaction proceeds was too slow to enable us to attain equilibrium in a reasonable time without the presence of a catalyst, the use of which we wished to avoid.

The relative rates of the two reactions during the initial stages are well shown in the experiments recorded below. A temperature of 850° was chosen as being that at which the reduction of carbon dioxide by carbon was fairly rapid, and the dissociation of carbon monoxide readily appreciable.

The rates of the reactions are calculated, by means of the relation

$$\frac{1}{t} \log \frac{C_o}{C_t} = k,$$

from the partial pressures (concentrations) of the carbon dioxide at different time intervals in experiment R 13, and from the partial pressures of the carbon monoxide in experiment R 15:

Experiment R 13.

$\text{CO}_2 + \text{C} = 2\text{CO}$. Temperature 850° .

| Time. (Unit=1 hour). | P . at 0° . | P_{CO} . | k_{CO} . |
|-------------------------|----------------------|-------------------|-------------------|
| 0 | 258.6 | 257.6 | — |
| 1 | 292.3 | 224.9 | 0.0590 |
| 2 | 317.8 | 199.4 | 0.0555 |
| 4 | 356.3 | 160.9 | 0.0511 |
| 6 | 389.0 | 128.2 | 0.0505 |
| 8 | 415.8 | 101.4 | 0.0506 |
| 12 | 439.5 | 77.7 | 0.0434 |

Experiment R 15.

$2\text{CO} = \text{CO}_2 + \text{C}$. Temperature 850° .

| Time. (Unit=1 hour). | P . at 0° . | P_{CO} . | k_{CO} . |
|-------------------------|----------------------|-------------------|-------------------|
| 0 | 463.0 | 453.7 | — |
| 24 | 459.2 | 446.1 | 0.00030 |
| 48 | 453.9 | 435.5 | 0.00037 |
| 72 | 452.1 | 431.9 | 0.00039 |
| 96 | 448.0 | 423.7 | 0.00031 |
| 120 | 447.2 | 422.1 | 0.00026 |

It will thus be seen that the reduction of carbon dioxide by carbon takes place at 850° at a speed 166 times as great as the dissociation of carbon monoxide at the same temperature.

We may incidentally draw attention to the fact that the good agreement of the constant k , calculated from the expression $\frac{1}{t} \log \frac{C_0}{C_t}$ for a unimolecular reaction, points to both reactions being essentially surface phenomena; the rate of reduction of carbon dioxide and the rate of dissociation of carbon monoxide both varying directly with the partial pressure of the gas. It is our intention to discuss this question more fully when we have concluded a research, on which we are at present engaged, on the relative rates of reaction between carbon dioxide, carbon monoxide, oxygen, and carbon at different temperatures.

This work has been undertaken in connexion with the experiments now being carried out by the Mining Association of Great Britain on coal-dust explosions. We are extending it to the investigation of the influence of pressure on the equilibrium ratio.

ALTONA.

CCXXVII.—*The Morphotropic Relationships between Silicon and Carbon Compounds of Corresponding Compositions.*

By GEORGE JERUSALEM.

CARBON occupies an altogether unique position amongst the elements in crystallographic as well as in chemical respects; although large numbers of compounds of the elements of group IV of the periodic classification have been crystallographically examined, no case has been yet observed in which a carbon atom is isomorphously replaced by one atom of any other element. It is true that both carbon tetraiodide and silicon tetraiodide crystallise in the cubic system, but, since the crystal class is known in neither case, the information requisite for deciding as to whether these two compounds are isomorphous is lacking. Isomorphism might be expected as between the metallic carbonates and metasilicates, but although comparison is possible in a number of cases, no instance is on record in which silicon replaces carbon without profound modification of the crystalline form; thus lithium carbonate, Li_2CO_3 , is monosymmetric with $a : b : c = 1.672 : 1 : 1.244$, $\beta = 114^\circ 25'$ (Mallard, *Zeitsch. Krist. Min.*, 1894, **23**, 483), whilst lithium metasilicate, Li_2SiO_3 , is rhombohedral with $a : c = 1 : 0.6681$ (Friedel, *Zeitsch. Krist. Min.*, 1903, **37**, 204). Comparison of the crystalline forms exhibited by the carbonates of the bivalent metals with those of the compounds CaSiO_3 , $\text{MgCa}(\text{SiO}_3)_2$, MgSiO_3 , MnSiO_3 , MgTiO_3 , MnTiO_3 , and FeTiO_3 , fails to reveal any isomorphous relationship between the carbonates and the latter compounds. Further, the observation that carborundum, CSi , is a stable substance dissimilar in crystalline form from either component element does not favour the view that the two elements are isomorphous.

Whilst a considerable amount of evidence, such as the above, indicates that carbon is crystallographically quite unique, it is noteworthy that ample evidence is available to show that silicon is displaceable by many bivalent elements without considerable change in crystalline form.

From a discussion of the crystal data available for carbon and silicon compounds, Barlow and Pope have been led to attribute the crystallographic—and also chemical—dissimilarity to a difference in the fundamental valencies of these two elements (*Trans.*, 1908, **93**, 1554); carbon thus stands alone as the only element exhibiting the fundamental valency of four, whilst silicon and many other elements are fundamentally bivalent. Owing to the comparative

case with which, during the last few years, it has become possible to exhibit the relation between chemical constitution and crystalline form, the question of the relative fundamental valencies of silicon and carbon has become one of great importance; the work described in the present paper was undertaken as a step towards the solution of the problem involved.

A study of the crystal data already available for corresponding silicon and carbon compounds indicates clearly that the two elements exercise such different morphotropic effects that few positive results could be hopefully anticipated unless some condition, hitherto unconsidered, were introduced for the purpose of accentuating such crystallographic similarity of function as may exist between silicon and carbon. The directing condition, thus indicated as desirable, is found in the rule discovered empirically by Tschermak (*Tsch. Min. Mitt.*, 1903, **22**, 393; *Ann. Reports*, 1908, **5**, 263) that, in the crystalline form of a compound substance, the principal axes of symmetry tend to express numerically the atomic composition of the molecule; thus, if three similar atoms are present with others in the molecule of a particular substance, the crystalline form of the compound will, in the majority of cases, include a three-fold axis of symmetry. Since crystal structures are now regarded as close-packed assemblages of atomic domains, a compound containing n identically located atoms, or groups of atoms, in the molecule would tend to exhibit a particular element of symmetry displaying an n -fold repetition; Tschermak's empirical rule has thus now acquired theoretical significance and, simultaneously, a concrete meaning. The rule may be conveniently applied to the purpose of accentuating any possible morphotropic relationship between two elements a and b , by preparing two substances containing in the molecule three large atomic groups or radicles associated with an a and b atom, respectively, of a unique kind; any morphotropy exhibited as between a and b should then be easily traced by goniometric examination.

This particular development of the new mode of regarding crystal structure is applied in the present paper to the examination of tribenzyl and triphenyl derivatives of silicol and carbinol; the introduction of three benzyl or phenyl groups into the molecule is, of course, intended to secure the presence of a trigonal axis of symmetry and to ensure that the silicon and carbon analogues shall to a very great extent exhibit identical marshalling of their component atoms.

Tribenzylsilicol, $(C_6H_5 \cdot CH_2)_3Si \cdot OH$.

A supply of this substance was kindly provided by Prof. F. S. Kipping, and melted at 106° , as stated by Dillthey (*Ber.*, 1905,

38, 4136). On slow evaporation of its solution in a mixture of chloroform and petroleum boiling at 70°, it was obtained in small, lustrous crystals suitable for measurement; the form {001} is the largest, and {100}, {101}, and {111}, although smaller, are well developed. The pyramid, {122}, is always very small but quite brilliant; no distinct cleavage was observed, but, as the faces of {111} are always much larger at one end of the *c*-axis, and as the faces of {122} are only observed at the same end of this axis, the substance is probably hemimorphous. No confirmation of the hemimorphism was obtained by the study of the etch-figures produced by the action of alcohol on faces of the form {001}.

Crystalline form: Orthorhombic.

$a : b : c = 1.7214 : 1 : 2.1384$.

Forms observed: {100}, {001}, {101}, {111}, and {122}.

The following angular measurements were obtained:

| Angles. | Number of observations. | Limits. | Mean. | Calculated. |
|--------------------|-------------------------|----------------|-------------|-------------|
| 111 : 111 | 16 | 55° 2'—55° 49' | 55° 30' 20" | — |
| 111 : 11 $\bar{1}$ | 14 | 43 46—44 15 | 44 1 50 | — |
| 111 : 100 | 33 | 61 31—62 54 | 62 13 0 | 62° 14' 50" |
| 101 : 001 | 13 | 50 59—51 35 | 51 18 30 | 51 10 0 |
| 001 : 122 | 4 | 65 31—66 6 | 65 53 0 | 65 48 50 |
| 101 : 100 | 9 | 38 26—39 6 | 38 47 0 | 38 59 0 |
| 122 : 122 | 1 | 48 23 | 48 23 0 | 48 22 20 |
| 111 : 001 | 9 | 67 43—68 17 | 68 1 50 | 67 59 0 |
| 101 : 111 | 4 | 53 16—53 27 | 53 19 10 | 53 17 10 |
| 100 : 122 | 10 | 74 51—75 20 | 75 7 50 | 75 15 30 |

It is very interesting to note that, although the substance does not exhibit a trigonal axis of symmetry as would be anticipated from Tschermak's empirical rule, it possesses a pseudo-trigonal axis, as would be expected from the interpretation of the rule and the molecular composition in accordance with Barlow and Pope's method. Thus, a crystal presenting trigonal symmetry, referred to rectangular axes, would exhibit as one axial ratio the value $1 : \sqrt{3} = 1 : 1.7321$, whilst an almost identical ratio, $b : a = 1 : 1.7214$, is actually observed on the crystals of tribenzylsilicol; the pseudo-trigonal nature of the crystal structure is thus apparent. It will be seen later that all the substances described below, in which three large groups are present in the molecular complex, conform to the same rule, and betray the presence of a trigonal or a pseudo-trigonal axis, with the possible exception of triphenylsilicol, of which the low crystal symmetry would naturally obscure the pseudo-trigonal character.

Taking the valency volume of silicon as two, that of tribenzylsilicol is $W = 110$, and the equivalence parameters are obtained as:

$$x : y : z = 5.3418 : 3.1032 : 6.6358,$$

The density of the crystalline substance was determined by Retgers' floating method in barium mercuri-iodide solution as $d=1.1772$, whence the molecular volume, $V=270.66$; the quotient, $R=V/H=2.4605$, and the molecular distance ratios are calculated as:

$$\chi:\psi:\omega=7.2116:4.1894:8.9586.$$

Tribenzylcarbinol, $(C_6H_5 \cdot CH_2)_3C \cdot OH$.

This substance was prepared by the method given by Klages and Heilmann (*Ber.*, 1904, **37**, 1456), and was obtained in crystals suitable for goniometric measurement by spontaneous evaporation of its solution in a mixture of chloroform and petroleum. The crystals so closely resemble those of the preceding compound that no separate description is necessary.

Crystalline system: Orthorhombic.

$$a:b:c=1.7166:1:2.1574.$$

Forms observed: {100}, {001}, {101}, {111}, and {122}.

The following angular measurements were obtained:

| Angles. | Number of observations. | Limits. | Mean. | Calculated |
|---------|-------------------------|---------------|-----------|------------|
| 100:111 | 26 | 61°52'—62°20' | 62° 8'50" | — |
| 001:111 | 22 | 68 0 —68 17 | 68 9 20 | — |
| 001:101 | 10 | 51 18 —51 37 | 51 26 50 | 51°28'10" |
| 100:101 | 13 | 38 21 —38 44 | 38 32 50 | 38 31 50 |
| 111:111 | 12 | 55 32 —55 51 | 55 37 10 | 55 42 20 |
| 111:111 | 18 | 43 31 —44 1 | 43 40 20 | 43 41 20 |
| 111:111 | 16 | 53 9 —53 36 | 53 20 50 | 53 19 30 |
| 100:122 | 12 | 74 51 —75 26 | 75 9 40 | 75 12 0 |
| 001:122 | 6 | 65 57 —66 7 | 66 2 10 | 65 59 20 |

The development of the faces indicates hemimorphous development as in the case of the corresponding silicic; the etch-figures obtained do not reveal hemimorphism. The axial ratios calculated show that the substance is very closely related morphotropically to the corresponding silicic, and the present observations constitute the first published evidence of morphotropy as between these two elements. The equivalent parameters are calculated as:

$$a:y:z=5.3482:3.1156:6.7215, \text{ with } H=112.$$

The density of the crystals was determined as $d=1.1869$, whence the molecular volume, $V=258.99$, and the quotient, $R=V/H=2.3124$. The molecular distance ratios are therefore:

$$\chi:\psi:\omega=7.0724:4.1200:8.8885.$$

Tribenzylmethyl Chloride, $(C_6H_5 \cdot CH_2)_3CCl$.

This substance was prepared by the method given by Schmerda (*Monatsh.*, 1909, **30**, 390), and exhibited the properties described

by him; it separates from its acetone solution in very small but quite brilliant rhombohedron-shaped crystals.

Crystalline system: Rhombohedral. Trapezohedral-tetartohedral class.

$a : c = 1 : 0.3700$.

Forms observed: $\{2\bar{1}10\}$ and $\{10\bar{1}1\}$.

The following angular measurements were obtained:

| Angles. | Number of Observations. | Limits. | Mean. | Calculated. |
|---------------------------|----------------------------|----------------------------------|----------------------|-----------------------|
| $2\bar{1}10 : 10\bar{1}1$ | 41 | $70^{\circ} 0' - 70^{\circ} 22'$ | $70^{\circ} 6' 20''$ | — |
| $10\bar{1}1 : 0\bar{1}11$ | 18 | $39 34 - 40 0$ | $39 49 20$ | $39^{\circ} 47' 20''$ |

The evidence that the crystals belong to the trapezohedral-tetartohedral class represented by quartz and cinnabar is, first, that the alternate faces of the form $\{2\bar{1}10\}$ are very different in size, and, secondly, that the etch-figures produced on these faces by the action of benzene are asymmetric with respect to the hexagonal planes of symmetry normal to the faces. A good cleavage is observed parallel to the form $\{2110\}$.

In order that the crystal form may be compared with those of the preceding compounds, it must first be stated with respect to the alternative hexagonal system and then referred to rectangular axes and the value, c/a , multiplied by five; the axial ratios are thus obtained in the form:

$a : b : c = 1.7321 : 1 : 2.1364$, and the equivalence parameters as:
 $x : y : z = 5.3656 : 3.0977 : 6.6180$, with $W = 110$.

The use of the factor five in the multiplication of the ratio c/a is naturally justified by the very close similarity which the equivalence parameters of the three above substances exhibit after the multiplication has been performed in the case of tribenzylmethyl chloride.

Triphenylsilicol, $(C_6H_5)_3Si \cdot OH$.

Triphenylsilicol was prepared by Dilthey and Eduardoff's method (*Ber.*, 1904, **37**, 1140), and showed the properties described by these authors; the best crystals were obtained from solutions in mixtures of chloroform and petroleum, but even these were poor, and scarcely suitable for goniometric examination. The forms $\{100\}$, $\{010\}$, and $\{001\}$ show the largest faces, and are about equally well developed; $\{111\}$ and $\{1\bar{1}1\}$ are very poorly developed, and unsatisfactory in character.

Crystalline system: Anorthic.

$a : b : c = 2.144 : 1 : 1.331$, $\alpha = 59^{\circ} 30'$, $\beta = 113^{\circ} 29'$, $\gamma = 84^{\circ} 11'$.

Forms observed: $\{100\}$, $\{010\}$, $\{001\}$, $\{111\}$, and $\{1\bar{1}1\}$.

The following angular measurements were obtained:

| Angles. | Number of observations. | Limits. | Mean. | Calculated. |
|---------|-------------------------|----------------|-------------|-------------|
| 100:001 | 16 | 58° 1'—58° 48' | 58° 20' 50" | — |
| 100:010 | 8 | 67 5 —67 46 | 67 25 0 | — |
| 001:010 | 10 | 52 50 —53 29 | 53 6 10 | — |
| 100:111 | 9 | 64 10 —64 47 | 64 29 30 | — |
| 111:001 | 9 | 90 33 —91 18 | 90 57 40 | — |
| 111:010 | 7 | 41 0 —41 58 | 41 39 10 | 42° 10' 20" |
| 111:001 | 5 | 61 56 —62 38 | 62 19 0 | 62 19 40 |
| 111:010 | 4 | 68 22 —68 53 | 68 36 30 | 69 2 20 |
| 111:100 | 2 | 58 57 —59 24 | 59 10 30 | 59 46 30 |

The density of the crystals was observed as $d=1.1777$, so that the molecular volume, $V=234.83$; the quotient, $R=V/W=2.5525$. No morphotropic relationship is immediately obvious between this and the previously described substances, and, since triphenylsilicic belongs to the anorthic system, the symmetry affords no indication as to the way in which a morphotropic relationship is to be sought; further, the ratio, V/W , is considerably larger than in the other cases referred to. It is consequently to be concluded that this silicic does not fall into line with the series now under discussion.

Triphenylcarbinol, (C₆H₅)₃C·OH.

This substance has already been crystallographically examined by Groth (*Zeitsch. Kryst. Min.*, 1881, **5**, 479), who found it to be rhombohedral with $a:c=1:0.6984$. Measurable crystals were obtained from benzene solution, and these showed only the forms {1011} and {1120}.

Crystalline system: Rhombohedral. $a:c=1:0.6975$.

The following angular measurements were obtained:

| Angles. | Number of Observations. | Limits. | Mean. | Calculated. |
|-----------|-------------------------|-----------------|------------|-------------|
| 210:1011 | 13 | 56° 46'—57° 19' | 57° 5' 40" | — |
| 1011:0111 | 5 | 65 35 —66 5 | 65 47 20 | 65° 48' 40" |

In order to render the crystal form comparable with those of the tribenzyl compounds described above, the ratio c/a must be multiplied by three and referred to a rectangular system of axes. The following ratios are thus obtained:

$$a:b:c=1.7321:1:2.0925.$$

$$x:y:z=5.1271:2.9601:6.1939; W=94.$$

The density of the crystals was determined as $d=1.1884$, so that the molecular volume, $V=218.92$, and the quotient, $R=V/W=2.3289$. The molecular distance ratios are:

$$\chi:\psi:\omega=6.7930:3.9236:8.2100.$$

The value for R is slightly greater than that for tribenzylcarbinol,

namely, 2.3124; this is in accordance with the indications obtained in the case of the picrates and styphnates. Aniline picrate gives an R value of 2.464, slightly greater than 2.433, the value for benzylamine picrate (Jerusalem, Trans., 1909, 95, 1290).

For comparison with the above substances the following crystalline forms may be quoted. Triphenylmethane is described as orthorhombic by Hintze with $a:b:c=0.5716:1:0.5867$ (*Zeitsch. Kryst. Min.*, 1884, 9, 546); on interchanging a and b , and multiplying the resulting value of c/b by two, the axial ratios become:

$$a:b:c=1.7495:1:2.0528.$$

ω -Bromotriphenylmethane, Ph_3CBr , was found to be hexagonal by Hintze (*loc. cit.*) with the value $a:c=1:0.7843$; on stating this ratio in the alternative hexagonal form as $a:c=1:0.6792$, multiplying c/a by three, and referring the ratio to rectangular axes, the values are obtained as:

$$a:b:c=1.7321:1:2.0376.$$

Triphenylacetic acid is monosymmetric (Groth, *Zeitsch. Kryst. Min.*, 1881, 5, 483), and the axial ratios can be stated in the form $a:b:c=0.5646:1:0.6161$, $\beta=90^\circ 12' 30''$ (Barlow and Pope, Trans., 1906, 89, 1719). On treating these axial ratios in the manner adopted with triphenylmethane, namely, multiplying c/b by two, and then interchanging a and b , the values become:

$$a:b:c=1.7712:1:2.1824, \alpha=90^\circ 12' 30''.$$

The additive compound of triphenylmethane and benzene, $(\text{C}_6\text{H}_5)_3\text{CH}\cdot\text{C}_6\text{H}_6$, is rhombohedral with $a:c=1:2.5565$ (Hintze, *loc. cit.*); by referring this ratio to rectangular axes it becomes:

$$a:b:c=1.7321:1:2.5565.$$

A consideration of the axial ratios, molecular distance ratios, and equivalence parameters for the above substances shows, first, that although the morphotropic relationships are distinctly evident in the axial ratios, they are much more completely expressed by the equivalence parameters. Secondly, it is obvious that the molecular distance ratios, although not greatly dissimilar in the instances in which they have been determined, differ much more amongst themselves than do the equivalence parameters; the degree with which they correspond is, in fact, measured in the main by the degree of approximation of the respective values of $R=V/W$. In this, as in the majority of other cases, the molecular distance ratios lend themselves less fruitfully to the discussion of morphotropic relationships than do the equivalence parameters; the morphotropy must therefore be considered merely in the light of the equivalence parameters, and the axial ratios and molecular distance ratios may be disregarded.

The following table states the equivalence parameters of all the substances dealt with above, calculated from the sets of axial ratios finally adopted. In the case of tribenzylsilicol, it is convenient to state the equivalence parameters in accordance with the alternatives that $Si=3$ and 4 :

| | x . | y . | z . | | |
|-------------------------------------|--------|--------|--------|---------|--------|
| 1. $(C_6H_5)_3CH_2Si\cdot OH$ | 5.3418 | 3.1032 | 6.6358 | $W=110$ | $Si=2$ |
| 2. $(C_6H_5)_3CH_2Si\cdot OH$ | 5.3740 | 3.1219 | 6.6758 | $W=112$ | $Si=4$ |
| 3. $(C_6H_5)_3CH_2C\cdot OH$ | 5.3482 | 3.1156 | 6.7215 | $W=112$ | |
| 4. $(C_6H_5)_3CH_2CCl$ | 5.3656 | 3.0977 | 6.6180 | $W=110$ | |
| 5. $(C_6H_5)_3C\cdot OH$ | 5.1271 | 2.9601 | 6.1935 | $W=94$ | |
| 6. $(C_6H_5)_3CH$ | 5.1572 | 2.9479 | 6.0515 | $W=92$ | |
| 7. $(C_6H_5)_3C\cdot Br$ | 5.1355 | 2.9651 | 6.0416 | $W=92$ | |
| 8. $(C_6H_5)_3C\cdot CO_2H$ | 5.2384 | 2.9576 | 6.4546 | $W=100$ | |
| 9. $(C_6H_5)_3CH_2C_6H_5$ | 5.2314 | 3.0203 | 7.7213 | $W=122$ | |

Considering the parameters 2 and 3, calculated on the basis that silicon and carbon both exhibit the fundamental valency 4, it is noticed that in passing from the silicol to the carbinol, the x -value diminishes by about one-half per cent., whilst the z -value increases by rather a larger fraction. If crystal structure is to be regarded as a question of close-packing, it is difficult to conceive that in the large tribenzylsilicol molecule the displacement of the silicon by a carbon atom of approximately the same valency volume four can lead, without change of symmetry, to such a notable change in dimensions of the packed structure; it seems thus indicated that carbon and silicon have not the same fundamental valency of four.

On considering next the values 1 and 3, calculated on the basis of $Si=2$ and $C=4$, it is seen that the differences for x and y are small, and that practically the whole weight of the displacement of

| | Differences | x . | y . | z . |
|---------|-------------|--------|--------|--------|
| 2 and 3 | | 0.0258 | 0.0063 | 0.0457 |
| 1 " 3 | " | 0.0061 | 0.0124 | 0.0857 |
| 3 " 4 | " | 0.0174 | 0.0179 | 0.1035 |
| 3 " 5 | " | 0.2211 | 0.1555 | 0.5280 |
| 5 " 6 | " | 0.0361 | 0.0122 | 0.1420 |
| 5 " 7 | " | 0.0087 | 0.0050 | 0.1519 |
| 5 " 8 | " | 0.1113 | 0.0025 | 0.1519 |
| 6 " 9 | " | 0.0742 | 0.0724 | 0.6698 |

silicon by carbon falls on the z -parameter, which thus changes by nearly 2 per cent.; this is in complete agreement with what would be anticipated by an increase of volume of one constituent atomic domain from 2 to 4. Such a substitution, provided that the mechanical operation of Tschermak's rule conserves the marshalling, could well lead to the expansion of the assemblage in one of the three rectangular directions of principal symmetry. An identical effect is, in fact, observed in operation in other cases, notably in the passage from tribenzylcarbinol to tribenzylmethyl chloride, where a similar change of valency volume by two units occurs as

the result of the displacement of the hydroxyl group by the chlorine atom; here again small changes occur in the values of two dimensions, x and y , and most of the weight of the substitution is thrown on to the third or z -parameter, which alters by about 1.5 per cent.

These considerations suggest that silicon and carbon have not the same fundamental valency, but that, whilst that of carbon is four, that of silicon is two. The available evidence is, however, not sufficient in amount to enable such a decision to be arrived at with certainty, but it must be concluded that the quantitative evidence, just as in the case of the humite series, points to the value of 2 rather than 4 as representing the fundamental valency of silicon.

The table of differences quoted makes it clear that the passage from tribenzylcarbinol to triphenylcarbinol, differences 3 and 5, is accompanied by a marked contraction of the structure in all three rectangular directions, but that this effect is much more marked in the direction of the z -dimension than in those of x and y . From differences 5 and 6, and 6 and 7, it is seen that the substitution of the hydroxyl group in triphenylcarbinol by hydrogen or bromine affects the crystal structure almost entirely in the direction of the z -axis; this is precisely what takes place in the corresponding operation of passing from tribenzylcarbinol to tribenzylsilicol, in which the valency volume was diminished by two units on the view that $\text{Si}=2$. The differences 5 and 8 show that the displacement of the hydroxyl group in triphenylcarbinol by carboxyl also produces a maximum effect in the z -dimension, although the dimension of x is also appreciably affected. The differences 6 and 9 indicate clearly that, in the passage from triphenylmethane to its addition compound with benzene, the dimensions of x and y are increased to an equal and small extent, whilst the main change in dimensions falls on the z -axis.

It is proposed to extend the application of Tschermak's rule to the investigation of morphotropy in later communications.

I desire to express my heartiest thanks to Prof. W. J. Pope, F.R.S., for having suggested this work, and for his kind help during its elaboration.

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CCXXVIII.—*Externally Compensated Tetrahydroquin-
alidine (Tetrahydro-2-methylquinoline) and its
Optically Active Components.*

By WILLIAM JACKSON POPE and JOHN READ.

THE resolution of externally compensated tetrahydroquin-
alidine (tetrahydro-2-methylquinoline) into its optically active components
was effected by Pope and Peachey (Trans., 1899, 75, 1066) by
crystallising its hydrochloride (two equivalents) with ammonium
d- α -bromocamphor- π -sulphonate (one equivalent) in aqueous solu-
tion; the deposit consists of practically pure *l*-tetrahydroquin-
alidine *d*- α -bromocamphor- π -sulphonate. The *d*-tetrahydroquin-
alidine was isolated from the mother liquors by fractional crystallisation of the
benzoyl derivative prepared from the separated crude *d*-base and
subsequent hydrolysis of the pure benzoyl-*d*-tetrahydroquin-
alidine. The method thus briefly described affords an easy method for the
preparation of *l*-tetrahydroquin-
alidine, but the isolation of the
enantiomorphously related base is lengthy and difficult; in the
present paper a method is described by means of which the two
enantiomorphously related bases can be readily prepared in a state of
high purity.

*Externally Compensated Tetrahydroquin-
alidine.*

This base was prepared, in the manner previously described, as
a colourless oil, boiling at 196°/207·5 mm.; at the ordinary tem-
perature it is a mobile liquid which shows no tendency to crystallise,
and, on cooling in boiling liquid air, it solidifies to a hard, resinous
material, which does not crystallise even after long exposure to the
low temperature thus obtained. When, however, a few drops of
the base are dissolved in ten times their volume of light petroleum,
and the solution cooled in boiling liquid air, tetrahydroquin-
alidine crystallises out as a mass of white needles; on inoculating carefully
purified externally compensated tetrahydroquin-
alidine with these
crystals at the ordinary temperature, crystallisation at once sets in,
and after the lapse of some hours the whole of the base becomes
converted into a hard, crystalline mass.

It is thus evident that at the ordinary laboratory temperature
externally compensated tetrahydroquin-
alidine is a supercooled liquid;
no other method than the one above described has yet been found
for causing the crystallisation. In all probability, the fact that
crystallisation can only be started by such an uncommon method
as that just described is responsible for the observation not having

been previously made that the modification of tetrahydroquinaldine stable at the ordinary temperature is a crystalline one.

A specimen of externally compensated tetrahydroquinaldine, prepared from a sample of the hydrochloride which had been repeatedly crystallised from acetone, after having been caused to crystallise in the manner indicated, melted at 20.75° ; after melting the crystalline mass, cooling it to 15° , and inoculating the liquid with the crystalline base, a standard thermometer immersed in the solidifying substance showed that the temperature rose to 20.75° during crystallisation. This may therefore be taken as the melting point of externally compensated tetrahydroquinaldine. It is interesting to note that on preserving a quantity of the crystalline material in contact with the liquefied substance at the laboratory temperature, the mass of minute crystals gradually becomes converted into several large rhombohedra; the latter grow to a diameter of four or five centimetres, and are very transparent, with highly plane faces. A good example is thus afforded of the well-known fact that the larger crystals present in contact with a solution tend to grow at the expense of the smaller ones (Curie, *Bull. Soc. Min. franç.*, 1885, 8, 145).

Preparation of Ammonium d- and l- α -Bromocamphor- π -sulphonates.

For the preparation of the large quantities of ammonium *d*- and *l*- α -bromocamphor- π -sulphonates required in this and similar work, the sulphonation with chlorosulphonic acid (Kipping and Pope, *Trans.*, 1895, 67, 356) is inconvenient, and may be replaced by a slight modification of the method first used by these authors (*Trans.*, 1893, 63, 577). A mixture of fuming and 100 per cent. sulphuric acids is made of such concentration that α -bromocamphor dissolves in it to a deep amber-coloured solution, and is not precipitated by pouring on to ice; the concentration of the acid used requires careful adjustment, and a suitable concentration was found to have the density 1.865 at 15° , and to consist of 200 c.c. of 100 per cent. sulphuric acid with 75 c.c. of 65 per cent. sulphur trioxide. This quantity of acid, cooled to the ordinary temperature, readily dissolves 95 grams of *d*- α -bromocamphor, and simultaneously the temperature rises to about 50° . After agitation for half a minute, the mixture is poured through a large funnel filled with crushed ice, when an insignificant separation of unchanged bromocamphor occurs; if the acid used is too concentrated, the sulphonation product suddenly carbonises with evolution of torrents of sulphur dioxide. It is convenient to sulphonate a kilogram of *d*- α -bromocamphor in quantities of 100 grams at a time, and almost to neutralise the diluted solution with milk of-lime, completing

the neutralisation with calcium carbonate; the solution is then run through a filter press, the filtrate treated with ammonium carbonate in the usual manner, again filtered, and the filtrate evaporated to crystallisation in large copper pans. The small amounts of copper which pass into solution are precipitated by ammonium sulphide; there should be taken that the lime, calcium carbonate, and water faced are free from chlorides, as the presence of ammonium chloride hinders the crystallisation of the ammonium bromocamphor-sulphonate.

The following determinations of rotatory power were made in aqueous solutions at 22° in 4-dm. tubes with ammonium salts which had been carefully purified by repeated crystallisation from water:

| Ammonium <i>d</i> - α -Bromocamphor- π -sulphonate. | | | Ammonium <i>l</i> - α -Bromocamphor- π -sulphonate. | | |
|--|-------------|------------|---|-------------|------------|
| 2.0139 grams in 50 c.c. | | | 2.0130 grams in 50 c.c. | | |
| Na(D line). | Hg(yellow). | Hg(green). | Na(D line). | Hg(yellow). | Hg(green). |
| α +13.94° | +14.72° | +17.30° | -13.62° | -14.47° | -16.97° |
| $[\alpha]$ +55.25 | +99.02 | +105.80 | -84.58 | -89.85 | -105.38 |
| Mean values: $[M]_D$ 273.69°; $[M]_{Hg(yellow)}$ 295.17°; $[M]_{Hg(green)}$ 316.55°. | | | | | |

The mean rotatory dispersions calculated from the above values are, for $Hg(green)/Na(yellow) = 1.243$, and for $Hg(yellow)/Na(yellow) = 1.059$; these constants are appreciably smaller than the corresponding ones for the camphor- β -sulphonic ions (Pope and Gibson, this vol., p. 2213). The values for the rotatory power for the *D*-line compare well with those determined by Kipping and Pope (Trans., 1893, 63, 589), namely, $[\alpha]_D + 84.78^\circ$ and $[M]_D + 278.25^\circ$.

By treating the ammonium salts with baryta as previously described (Pope and Peachey, Trans., 1898, 73, 893), solutions of the pure optically active acids can be obtained.³ The silver α -bromocamphor- π -sulphonates are easily obtained by saturating the solutions of the acids with silver hydroxide, filtering, and evaporating to crystallisation; this method is far more convenient than the one recommended by Meisenheimer (Ber., 1908, 41, 3973).

Resolution of Externally Compensated Tetrahydroquinaldine.

On treating racemic tetrahydroquinaldine hydrochloride with rather less than half an equivalent of ammonium *d*- α -bromocamphor- π -sulphonate, as already described (Trans., 1899, 75, 1066), the greater part of the *l*-base separates as the sparingly soluble *l*-tetrahydroquinaldine *d*- α -bromocamphor- π -sulphonate; the latter salt is obtained in a state of high purity by crystallisation from alcohol. The mother liquors, containing the whole of the *d*-base, are then treated with sodium hydroxide, the base separated, and distilled;

the rotatory power of the distillate is then determined, and the percentage of *d*-base calculated; in general, about 80 per cent. of *d*-base is present. This base is next dissolved in the requisite amount of dilute hydrochloric acid, and to the hot solution is added ammonium *l*- α -bromocamphor- π -sulphonate; the proportion of the latter used is about 2 per cent. less than the quantity equivalent to the *d*-tetrahydroquinaldine present. Crystallisation does not ordinarily occur spontaneously, but may be induced by inoculation with a little crystalline *d*-tetrahydroquinaldine *l*- α -bromocamphor- π -sulphonate; the latter is readily obtained by evaporating a few drops of the solution to dryness, and rubbing the residue with ether. After inoculation, crystallisation takes place with considerable rise in temperature, and almost the whole of the *d*-base separates as the salt of the optically active acid; the salt is purified by crystallisation from boiling alcohol, and its physical properties correspond with those of the enantiomorphously related salt.

The base extracted from the final mother liquors consists mainly of *l*-tetrahydroquinaldine, which may be separated by again treating with ammonium *d*- α -bromocamphor- π -sulphonate in hydrochloric acid solution. The practically quantitative separation of the externally compensated tetrahydroquinaldine into its optically active components is thus effected.

1-(*d*-)Tetrahydroquinaldine and 1-(*l*-) α -Bromocamphor- π -sulphonate.

These salts, which crystallise in long, colourless needles, melting at 218–220°, exhibit distinct mutarotation in absolute alcoholic solution, but since the solutions, which are at first colourless, rapidly become brown, no trustworthy quantitative determinations of the mutarotation have yet been made. The observed values of the specific rotatory powers in 0.8 per cent. alcoholic solutions at 20° were:

$[\alpha]_D^{20}$ 37.0° to 41.4°, $[\alpha]_{Hg(yellow)}^{20}$ 39.2° to 43.0°, and $[\alpha]_{Hg(green)}^{20}$ 49.5° to 52.3°.

The solutions in water remain colourless, and no mutarotation was observed; the following values were obtained in 4-dm. tubes at 17°:

| l-Base, d-Acid. | | | d-Base, l-Acid. | | |
|---|-------------|------------|------------------------|-------------|------------|
| 0.2118 gram in 30 c.c. | | | 0.2034 gram in 30 c.c. | | |
| Na(D line). | Hg(yellow). | Hg(green). | Na(D line). | Hg(yellow). | Hg(green). |
| α + 0.91° | + 0.95° | + 1.14° | - 0.87° | - 0.92° | - 1.05° |
| $[\alpha]$ + 32.22 | + 33.99 | + 40.37 | - 32.08 | - 33.92 | - 40.19 |
| Mean values: $[\alpha]_D$ 137.34°; $[\alpha]_{Hg(yellow)}$ 155.61°; $[\alpha]_{Hg(green)}$ 184.00°. | | | | | |

The rotatory dispersions calculated from the above values are, for $Hg(green)/Na(yellow) = 1.253$, and for $Hg(yellow)/Na(yellow) = 1.056$.

1- and d-Tetrahydroquinaldine.

The optically active bases were obtained by treating the above-described salts with alkali, and distilling the separated oil under diminished pressure. On cooling in boiling liquid air, they solidify to colourless resins, which show no tendency to crystallise; when a few drops of one of the active bases are dissolved in light petroleum and cooled in boiling liquid air, crystallisation occurs, but the crystalline material thus obtained does not cause the crystallisation of the *d*- or *l*-base when used for inoculation at any temperature which could be established. It thus appears that the optically active tetrahydroquinaldines crystallise at a temperature far below the ordinary one, whilst the racemic substance crystallises at 20-75°; a somewhat similar case is presented by the active and inactive methyl methoxysuccinates (Purdie and Neave, this vol., p. 1518).

The following determinations of rotatory power were made in 1-dm. tubes, and the formula deduced by Pope and Peachey (Trans., 1899, 75, 1114) as connecting the density and temperature of the bases was used in calculating the specific rotatory powers:

| <i>d</i> -Tetrahydroquinaldine at 16°. | | | <i>l</i> -Tetrahydroquinaldine at 20°. | | |
|--|--------------|-------------|--|--------------|-------------|
| NaD (line). | Hg (yellow). | Hg (green). | NaD (line). | Hg (yellow). | Hg (green). |
| α +61.13° | +63.66° | +71.85° | -61.20° | -63.80° | -71.97° |
| $[\alpha]$ +40.79 | +62.26 | +70.27 | -60.04 | -62.59 | -70.61 |

The mean rotatory dispersions are, for $Hg_{(green)}/Na_{(yellow)} = 1.176$, and for $Hg_{(yellow)}/Na_{(yellow)} = 1.042$.

The purest specimen of *l*-tetrahydroquinaldine obtained by Pope and Peachey gave the specific rotatory power $[\alpha]_D -58.12^\circ$, which is slightly lower than the values now recorded. Ladenburg, who resolved the externally compensated base by crystallisation with tartaric acid, obtained *l*-tetrahydroquinaldine with a rotatory power in a 1-dm. tube of $\alpha_D -50.38^\circ$ (Ber., 1894, 27, 78), and, with the aid of *l*-tartaric acid, has recently obtained *d*-tetrahydroquinaldine with $\alpha_D +50.58^\circ$ (Ladenburg and Hermann, Ber., 1908, 41, 966). As we now show that the optically active tetrahydroquinaldines have a rotatory power of $\alpha_D 61.13^\circ$ to 61.20° in 1-dm. tubes, it appears that Ladenburg's purest specimens of the active bases contained about 5 per cent. of the enantiomorphously related isomerides.

Although the optically active bases could not be caused to crystallise, a mixture of equal weights of each crystallised readily when inoculated with a crystal of the racemic base.

d-(*l*)-Tetrahydroquinaldine *d*-(*l*)- α -Bromocamphor- π -sulphonate.

On dissolving pure *d*-tetrahydroquinaldine in the equivalent quantity of *d*- α -bromocamphor- π -sulphonic acid solution and

evaporating to dryness, a gummy residue is obtained, which crystallises when rubbed in contact with dry ether. After crystallisation from ethyl acetate, the salt is obtained in small, colourless needles, melting at 162–165°. It is very soluble in water or alcohol, but less so in ethyl acetate. The salt which is enantiomorphously related to the foregoing is obtained in a similar manner, and it is noteworthy that the crystallisation of either salt is induced by inoculation with a crystal of the other:

0.0995, dried at 100°, gave 0.1903 CO₂ and 0.0548 H₂O. C=52.16; H=6.16.

C₂₀H₂₈O₄NBrS requires C=52.37; H=6.16 per cent.

The salts behave similarly to their two isomerides in alcoholic solution, and exhibit mutarotation, which could not be accurately determined owing to the gradual darkening of the solutions on preservation; the observed specific rotatory powers varied between [α]_D 96° and 101°, [α]_{Hg (yellow)} 101° and 107°, and [α]_{Hg (green)} 118° and 124° in 1 per cent. solutions.

The following determinations were made in aqueous solutions at 17° in 4-dm. tubes:

| <i>d</i> -Base, <i>d</i> -Acid. | | | <i>l</i> -Base, <i>l</i> -Acid. | | |
|---------------------------------|------------|-----------|---------------------------------|------------|-----------|
| 0.2143 gram in 30 c.c. | | | 0.2082 gram in 30 c.c. | | |
| Na(D line) | Hg(yellow) | Hg(green) | Na(D line) | Hg(yellow) | Hg(green) |
| α +2.50° | +2.61° | +3.05° | α -2.42° | -2.54° | -2.86° |
| [α] +87.49 | +91.34 | +106.74 | [α] -87.18 | -91.50 | -106.63 |

Mean values: [M]_D 490.2°; [M]_{Hg (yellow)} 419.0°; [M]_{Hg (green)} 488.9°.

The mean rotatory dispersions in aqueous solution are, for Hg(green)/Na(yellow)=1.222, and for Hg(yellow)/Na(yellow)=1.047.

d- and *l*-Tetrahydroquinaldine Hydrochloride, C₁₀H₁₃N, HCl, H₂O.

For comparison with the salts with optically active acids, it seemed desirable to determine the rotatory powers of the hydrochlorides prepared from pure *d*- and *l*-tetrahydroquinaldine; these salts were prepared as already described, and recrystallised from acetone. The following determinations were made in aqueous solution in 4-dm. tubes at 17°:

Hydrochloride of d-Base.

| Weight in 30 c.c. | | Na(D line) | Hg(yellow) | Hg(green) |
|-------------------|-----|------------|------------|-----------|
| 0.1111 gram | α | + 0.99° | + 1.02° | + 1.17° |
| | [α] | 66.83 | 68.86 | 78.98 |
| 0.2064 " | α | 1.78 | 1.84 | 2.10 |
| | [α] | 66.62 | 68.86 | 78.79 |
| 0.4116 " | α | 3.64 | 3.78 | 4.31 |
| | [α] | 66.33 | 68.88 | 78.53 |

Hydrochloride of I-Base.

| Weight in 80 c.c. | | Na(D line). | Hg(yellow). | Hg(green). |
|-------------------|------------|-------------|-------------|------------|
| 0.1196 gram | α | -1.01° | -1.05° | -1.20° |
| | $[\alpha]$ | 66.68 | 69.32 | 79.23 |
| 0.2062 " | α | 1.83 | 1.90 | 2.18 |
| | $[\alpha]$ | 66.56 | 69.11 | 79.29 |
| 0.4017 " | α | 3.56 | 3.70 | 4.23 |
| | $[\alpha]$ | 66.47 | 69.80 | 78.98 |

Mean molecular rotatory powers: $[M]_D$ 134.24°; $[M]_{Hg}$ (yellow) 139.15°; $[M]_{Hg}$ (green) 159.14°.

The mean rotatory dispersions are, for $Hg(green)/Na(yellow) = 1.186$, and for $Hg(yellow)/Na(yellow) = 1.037$.

It will be seen that the values for the two hydrochlorides agree very closely, and that the specific rotatory power decreases slowly as the concentration increases. The mean values are appreciably higher than were obtained by Pope and Peachey, who found the value $[M]_D -121.7^\circ$ for *l*-tetrahydroquinaldine hydrochloride in dilute aqueous solution.

From the values now recorded, the molecular rotatory powers of the optically active basic and acidic ions can be calculated for comparison with those directly observed with the tetrahydroquinaldine hydrochlorides and the ammonium α -bromocamphor- π -sulphonates by means of the formulae:

$$[M] \text{ of } dBdA + [M] \text{ of } lBdA = \text{Twice } [M] \text{ of } dA \text{ ion.}$$

$$[M] \text{ of } dBdA - [M] \text{ of } lBdA = \text{Twice } [M] \text{ of } dB \text{ ion.}$$

The following values are thus calculated:

| <i>Basic ion.</i> | | | <i>Acidic ion.</i> | | |
|---|-------------|------------|--------------------|-------------|------------|
| Na(D line). | Hg(yellow). | Hg(green). | Na(D line). | Hg(yellow). | Hg(green). |
| $[M]$ 126.4 | 131.7 | 152.2° | | 273.8° | 337.8° |
| Dispersions: $Hg(green)/Na(yellow) = 1.203$; $Hg(green)/Na(yellow) = 1.230$; $Hg(yellow)/Na(yellow) = 1.041$; $Hg(yellow)/Na(yellow) = 1.049$. | | | | | |

The appended values are those deduced from the examination of the hydrochlorides of the base and the ammonium salts of the optically active acids:

| Na(D line). | Hg(yellow). | Hg(green). | Na(D line). | Hg(yellow). | Hg(green). |
|---|-------------|------------|-------------|-------------|------------|
| $[M]$ 134.2° | 139.1° | 159.1° | | 278.7° | 346.6° |
| Dispersions: $Hg(green)/Na(yellow) = 1.186$; $Hg(green)/Na(yellow) = 1.243$; $Hg(yellow)/Na(yellow) = 1.037$; $Hg(yellow)/Na(yellow) = 1.059$. | | | | | |

It is noteworthy that, although the molecular rotatory powers and dispersions calculated in the two different ways respectively are of the same order, the differences are much greater than could be attributed to experimental error. The discrepancies are scarcely traceable to the disregard of the concentration of the solutions

examined, and are possibly due to the operation of isomeric change (compare Kipping, *Trans.*, 1906, **87**, 628); the whole question is now being further studied.

The Optically Active Benzoyltetrahydroquinaldines.

With the aid of the pure optically active tetrahydroquinaldines which have been now prepared, it is possible to obtain the benzoyl derivatives in a greater state of purity than previously, and to make standard measurements of their rotation constants; these are of interest because the sign of rotation of the base changes during preparation of the benzoyl derivative. The benzoyl derivatives were prepared in the manner already described, and the following determinations made in absolute alcoholic solution in 4-dm. tubes:

Benzoyl-d-tetrahydroquinaldine.

| Weight in 30 c.c. | <i>t.</i> | | Na(D line). | Hg(yellow). | Hg(green). |
|-------------------|-----------|--------------|-------------|-------------|------------|
| 0.1602 gram | 17° | α | - 7.03° | - 7.40° | - 8.59° |
| | | [α] | 329.1 | 346.4 | 402.1 |
| 0.5031 gram | 18 | α | 21.93 | 23.00 | 26.68 |
| | | [α] | 326.9 | 342.9 | 397.7 |

Benzoyl-l-tetrahydroquinaldine.

| | | | | | |
|-------------|-----|--------------|---------|---------|---------|
| 0.1751 gram | 17° | α | + 7.70° | + 8.06° | + 9.40° |
| | | [α] | 329.3 | 346.1 | 402.6 |
| 0.5067 gram | 18 | α | 22.07 | 23.12 | 26.84 |
| | | [α] | 326.7 | 342.2 | 397.3 |

The agreement between the specific rotatory powers of the *d*- and *l*-isomerides for similar concentration and identical wave-length is very close. The mean specific rotatory powers are, for the lower concentration at 17°:

$$[\alpha]_D 329.46^\circ; [\alpha]_{Hg(yellow)} 346.26^\circ; [\alpha]_{Hg(green)} 402.38^\circ.$$

The rotatory dispersions are, for $Hg(green)/Na(yellow) = 1.221$, and for $Hg(yellow)/Na(yellow) = 1.051$.

For the higher concentration at 18°, the mean values are:

$$[\alpha]_D 326.79^\circ; [\alpha]_{Hg(yellow)} 342.54^\circ; [\alpha]_{Hg(green)} 397.50^\circ.$$

The rotatory dispersions are, for $Hg(green)/Na(yellow) = 1.217$, and for $Hg(yellow)/Na(yellow) = 1.048$.

In view of the obvious high order of accuracy of the above determinations, it can be safely concluded that the rotatory dispersions of the benzoyl derivatives diminish slightly as the concentration increases, and that the rotatory dispersions of the benzoyl derivatives and those of the parent bases are not identical.

CCXXIX.—*The Resolution of Externally Compensated Pavine and α -Bromocamphor- π -sulphonic Acid.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

PYMAN has recently demonstrated the probability (Trans., 1909, 95, 1610) that the "tetrahydropapaverine" described by Goldschmidt (*Monatsh.*, 1886, 7, 485; 1898, 19, 324) is the 1:2-dihydropapaverine; some little uncertainty still remains as to the constitution of Goldschmidt's base, and Pyman and Reynolds (this vol., p. 1320) consequently prefer to call the substance pavine. The presence of an asymmetric carbon atom in the molecule of "tetrahydropapaverine," or pavine, was demonstrated by the resolution of the base into its optically active components (Pope and Peachey, Trans., 1898, 73, 893), but in view of the interest which now attaches to pavine it seemed desirable to apply to its resolution the methods which have been developed since that date.

Preparation of Externally Compensated Pavine.

The method of reducing papaverine described by Pyman yields the true tetrahydropapaverine as the chief product; the following process furnishes good yields of pavine. Papaverine (35 grams), hydrochloric acid (480 c.c.), and water (800 c.c.) are heated together under reflux, powdered tin (95 grams) being added in small portions; the tin becomes completely dissolved after about twenty hours' boiling, and, on cooling, a white, crystalline double salt separates. The latter is crystallised once from boiling water, and freed from tin by precipitation with hydrogen sulphide in boiling aqueous solution; the filtered solution, on evaporation, yields pavine hydrochloride, which is purified by crystallisation from hot water. About one-quarter of the papaverine used is thus obtained as pavine, whilst the mother liquors contain both the latter base and tetrahydropapaverine. This considerable yield of pavine is of interest in connexion with the suggestion, made and rejected by Pyman and Reynolds (*loc. cit.*), that this base is formed from some impurity present in the papaverine used.

Resolution of Externally Compensated Pavine.

The resolution of pavine into its optically active components, by crystallising the externally compensated base with one equivalent of α -bromocamphor- π -sulphonic acid, as described by Pope and Peachey, proceeds slowly, because the sparingly soluble crystalline salt of the *l*-component and the resinous salt of the *d*-component

component separate together; the former salt is with difficulty purified from the latter by crystallisation. The following application of Pope and Peachey's method (Trans., 1899, 75, 1066) leads to a more satisfactory resolution of the base into its optically active components.

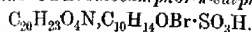
Externally compensated pavine hydrochloride is treated with one-half an equivalent proportion of ammonium *d*- α -bromocamphor- π -sulphonate in hot aqueous solution; on cooling, *l*-pavine *d*- α -bromocamphor- π -sulphonate separates in long needles not contaminated by the resinous salt of the *d*-base. That the salt *l*BdA thus obtained contained none of the salt *d*BdA was shown by treating it, without recrystallisation, with ammonia, and determining the specific rotatory power of the liberated base; in an 8 per cent. chloroform solution the value $[\alpha]_D - 152.0^\circ$ was obtained, which agrees well with the more accurately determined constant given below. It is clear that the resolution proceeds in accordance with the first type distinguished by Pope and Read (this vol., p. 989).

Although the separation of a pure *l*-pavine salt is rendered easy by the above method, yet the yield is not large, because on working in concentrated solutions, or on concentrating the mother liquors, hydrochloride of the base crystallises together with the salt *l*BdA; the following modification of the original process, which is applicable in other cases, was therefore adopted. The salts formed by pavine with inorganic acids are in general sparingly soluble in water, but Pope and Peachey found that the *d*-camphor- β -sulphonates of the base are readily soluble in water (Trans., 1898, 73, 902); the externally compensated pavine was therefore dissolved in one equivalent proportion of *d*-camphor- β -sulphonic acid, and to the solution was added half an equivalent of ammonium *d*- α -bromocamphor- π -sulphonate, water being used as the solvent, and the solution being kept as concentrated as conveniently possible. Of the number of salts which might be formed in the mixed solution, *l*-pavine *d*- α -bromocamphor- π -sulphonate is the least soluble, and, as only sufficient ammonium salt was added to allow of the formation of this salt, it was to be expected that practically the whole of the *l*-pavine would separate as the pure salt. In accordance with this anticipation, the solution, prepared as described above, deposited almost all of the *l*-pavine as the sparingly soluble *d*- α -bromocamphor- π -sulphonate, and the deposited salt, after once recrystallising from boiling aqueous alcohol, has the properties previously ascribed to it.

After the *l*-pavine *d*- α -bromocamphor- π -sulphonate has been obtained in a pure state, the residual base—consisting almost entirely of *d*-pavine—is precipitated from the mother liquors by addition of

ammonia, and its actual content of *d*-pavine determined from its rotatory power in chloroform solution; the base is then dissolved in the requisite amount of *d*-camphor- β -sulphonic acid solution, and ammonium *l*- α -bromocamphor- π -sulphonate added in just sufficient quantity to precipitate all the *d*-pavine as the salt *dB*/A, which, being enantiomorphously related to the crystalline salt *lBd*/A dealt with above, exhibits ordinary physical properties identical with those of the latter.

d-Pavine 1- α -Bromocamphor- π -sulphonate,



This new salt separates immediately in long, colourless needles when the above operation is performed; after cooling, the salt is collected and recrystallised from boiling aqueous alcohol. The substance decomposes at 290–300°, and gave the following results on analysis:

0.0933 gave 0.1898 CO_2 and 0.0482 H_2O . C=55.19; H=5.78.

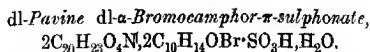
$\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_2\text{BrS}$ requires C=55.19; H=5.87 per cent.

d- and *l*-Pavine.

These substances separate on cooling a hot dilute alcoholic solution of the corresponding bromocamphorsulphonates after addition of ammonia; after recrystallisation from benzene, the bases melted at 224°. The following determinations of rotatory power were made with the recrystallised substances after drying at 110°:

| <i>l</i> -Pavine. | | | <i>d</i> -Pavine. | | |
|--|-------------|------------|--|-------------|------------|
| 0.1833 gram, made up to 20 c.c. with chloroform, in a 2-dm. tube at 23°: | | | 0.1970 gram, made up to 20 c.c. with chloroform, in a 2-dm. tube at 23°: | | |
| Na(D line). | Hg(yellow). | Hg(green). | Na(D line). | Hg(yellow). | Hg(green). |
| α - 2.960 | - 3.119° | - 3.500° | α + 2.960° | + 3.093° | + 3.470° |
| [α] - 150.3 | - 157.3 | - 176.5 | [α] + 150.3 | + 157.0 | + 176.1 |
| 0.7316 gram, made up to 20 c.c. with chloroform, in a 1-dm. tube at 22°: | | | 0.7033 gram, made up to 20 c.c. with chloroform, in a 1 dm. tube at 22°: | | |
| α - 5.445° | - 5.730° | - 6.500° | α + 5.241° | + 5.520° | + 6.250° |
| [α] - 149.8 | - 156.6 | - 177.7 | [α] + 149.0 | + 157.0 | + 177.7 |

The values obtained under similar conditions for the two enantiomorphously related bases are in good agreement, and are slightly higher than those previously recorded; the specific rotatory power diminishes slowly with increasing concentration, and the numbers afford some indication that the rotatory dispersion is dependent on the concentration of the solution.



In view of the sparing solubility of the two crystalline salts dealt with above, namely, *l*BdA and *d*B/A, and of the fact that the salts *d*BdA and *l*B/A are resinous and also sparingly soluble, it seemed desirable to examine the salt formed by externally compensated pavine with the externally compensated α -bromocamphor- π -sulphonic acid. This substance was easily prepared by dissolving *dl*-pavine in an aqueous solution of the requisite amount of *dl*- α -bromocamphor- π -sulphonic acid, and evaporating to a gummy consistency; the residue crystallises on keeping, and after several recrystallisations from strong alcohol the salt is obtained in radiate clusters of soft, white, silky needles. The salt is optically inactive in aqueous solution, and the following analyses were made on the air-dried material:

0.1111 gave 0.2204 CO₂ and 0.0595 H₂O. C=54.11; H=5.97.
 0.3233, heated at 110° for three hours, lost 0.0044. H₂O=1.33.
 C₆₀H₇₆O₁₆N₂Br₂S₂H₂O requires C=54.44; H=5.94;
 H₂O=1.36 per cent.

This fully racemic salt thus differs from the active ones previously described, which crystallise without water, in containing water of crystallisation; it is also very soluble in water, and melts without blackening at 248–250°, whilst the active salts are sparingly soluble and decompose at 290–300°.

The Resolution of Externally Compensated α -Bromocamphor- π -sulphonic Acid.

The ease with which the resolution of externally compensated pavine can be effected with the aid of *d*- and *l*- α -bromocamphor- π -sulphonic acid suggests that the optically active bases could be used in effecting the resolution of the externally compensated acid in accordance with the method of Pope and Peachey.

With this object, an aqueous solution was prepared containing *d*-pavine (one equivalent), ammonia (one equivalent), and *dl*- α -bromocamphor- π -sulphonic acid; a clear solution is obtained on boiling with addition of a little alcohol, and, on cooling, the greater part of the alkaloid separates as the crystalline *d*-pavine *l*- α -bromocamphor- π -sulphonate. After recrystallisation from water, the latter salt was treated with ammonia, and the resulting ammonium *l*- α -bromocamphor- π -sulphonate separated by crystallisation; 0.1080 gram of this ammonium salt, made up to 20 c.c. with water, gave $\alpha_D - 0.915^\circ$ in a 2-dm. tube at 22°, whence $[\alpha]_D - 84.7^\circ$. The latter

value is identical with that observed with ammonium *l*- α -bromocamphor- π -sulphonate prepared from *l*-camphor, so that the resolution of the externally compensated acid has been effected.

The mother liquors from which the *d*-pavine salt had been separated were next treated with ammonia, filtered, and evaporated until crystallisation occurred; on recrystallising the residue from aqueous alcohol, pure ammonium *d*- α -bromocamphor- π -sulphonate was obtained. 0.1082 gram, made up to 20 c.c. with water, gave $\alpha_D + 0.915^\circ$ in a 2-dm. tube at 22° , whence $[\alpha]_D + 84.6^\circ$, which is the value ordinarily assigned to pure ammonium *d*- α -bromocamphor- π -sulphonate.

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CCXXX.—*The Rotatory Powers of the Salts of d- and l-Camphor- β -sulphonic Acid with d- and l-Pavine.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

It has been repeatedly shown that a knowledge of molecular rotatory power in aqueous solution renders great service in connexion with the resolution of externally compensated bases (or acids) by crystallisation with a powerful optically active acid (or base); the theoretical scheme which leads to the indicated use of rotatory power determinations is too well known to require recapitulation (see preceding paper). At the same time, the experimental data on which the scheme is based are not very extensive, and it is of importance to collect further evidence in justification of the extended use now so frequently made of determinations of molecular rotatory powers in aqueous solutions. For this reason, we have made a careful polarimetric examination of the *d*- and *l*-pavine *d*- and *l*-camphor- β -sulphonates, and have appended thereto a description of a number of metallic salts of the latter acids.

d-Pavine *d*-Camphor- β -sulphonate and *l*-Pavine *l*-Camphor- β -sulphonate, $C_{20}H_{23}O_4N, C_{10}H_{15}O \cdot SO_3H$.

These salts are obtained by boiling equivalent quantities of the silver salt of the corresponding acid with the hydrochloride of the corresponding base in aqueous solution; after filtration and concentration, they are obtained crystalline, and, on recrystallisation

from hot alcohol, separate in glistening clusters of colourless, transparent prisms. They are very soluble in water or hot alcohol, less so in acetone or cold alcohol, and almost insoluble in benzene or ether, and do not melt on heating:

0.1156 of *d*-salt gave 0.2656 CO₂ and 0.0708 H₂O: C=62.67; H=6.85.

0.1175 of *l*-salt gave 0.2694 CO₂ and 0.0726 H₂O. C=62.39; H=6.93.

C₃₀H₃₈O₈NS requires C=62.78; H=6.86 per cent.

The following determinations of rotatory power were made in 2-dcm. tubes at 21°, water being used as the solvent:

| <i>dBdA.</i> | | | | <i>lB/A.</i> | | | |
|------------------------|-------------|------------|--|------------------------|-------------|------------|--|
| 0.1091 gram in 20 c.c. | | | | 0.1142 gram in 20 c.c. | | | |
| Na(D line). | Hg(yellow). | Hg(green). | | Na(D line). | Hg(yellow). | Hg(green). | |
| α +1.372° | +1.454° | +1.663° | | -1.438° | -1.510° | -1.733° | |
| [α] +125.4 | +132.9 | +152.0 | | -125.9 | -132.2 | -151.7 | |
| [M] +718.7 | +761.5 | +871.0 | | -721.5 | -757.5 | -869.3 | |

From the above values the mean molecular rotatory powers of the salts *dBdA* and *lB/A* in dilute aqueous solution are calculated as $[M]_D \pm 720.1^\circ$, $[M]_{Hg(yel.)} \pm 759.5^\circ$, and $[M]_{Hg(green)} \pm 870.1^\circ$. The molecular rotatory dispersions are for $Hg(green)/Na(yellow) = 1.208$, and for $Hg(yellow)/Na(yellow) = 1.055$.

d-Pavine 1-Camphor- β -sulphonate and *l*-Pavine *d*-Camphor- β -sulphonate, *dB/A* and *lBdA*.

These salts were prepared and crystallised in the same way as the two preceding ones, from which they differ but little in solubilities and general physical properties; they crystallise in small, colourless needles:

0.1189 *dB/A* gave 0.2726 CO₂ and 0.0716 H₂O. C=62.53; H=6.74.

0.1033 *lB/A* .. 0.2370 CO₂ .. 0.0645 H₂O. C=62.57; H=6.98.

C₃₀H₃₈O₈NS requires C=62.78; H=6.86 per cent.

The following determinations of rotatory power were made in 2 dcm. tubes at 20°, water being the solvent:

| <i>dB/A.</i> | | | | <i>lBdA.</i> | | | |
|------------------------|-------------|------------|--|------------------------|-------------|------------|--|
| 0.1200 gram in 20 c.c. | | | | 0.1228 gram in 20 c.c. | | | |
| Na(D line). | Hg(yellow). | Hg(green). | | Na(D line). | Hg(yellow). | Hg(green). | |
| α +1.315 | +1.365° | +1.540° | | -1.340° | -1.380° | -1.580° | |
| [α] +109.6 | +113.8 | +128.3 | | -109.3 | -113.6 | -128.9 | |
| [M] +628.1 | +652.1 | +735.1 | | -626.3 | -651.0 | -738.6 | |

The mean molecular rotatory dispersions of the salts *dB/A* and *lBdA* in dilute aqueous solution are hence calculated as:

$[M]_D \pm 627.2^\circ$, $[M]_{Hg(yel.)} \pm 651.5^\circ$, and $[M]_{Hg(green)} \pm 736.8^\circ$.

The molecular rotatory dispersions are for $Hg_{(green)}/Na_{(yellow)} = 1.175$, and for $Hg_{(yellow)}/Na_{(yellow)} = 1.039$; these values differ considerably from the corresponding rotatory dispersions for the salts $dBdA$ and lBA , and this, as will be shown below, is to be traced to the differences in molecular rotatory dispersion between the basic and the acid ions.

It has been shown by Pope and Peachey (Trans., 1899, 75, 1084) that the molecular rotatory powers of the basic and acidic ions may be calculated in the following manner from the molecular rotatory powers of the salts $dBdA$ and lBA in dilute aqueous solutions:

$$[M] \text{ of } dBdA + [M] \text{ of } lBA = \text{Twice } [M] \text{ of } dB \text{ ion.}$$

$$[M] \text{ of } dBdA - [M] \text{ of } lBA = \text{Twice } [M] \text{ of } dA \text{ ion.}$$

Applying these formulæ to the values given above, the following are obtained:

| Molecular rotations. | | | Rotatory dispersions. | |
|----------------------|-----------------|-----------------------------|---------------------------|----------------------------|
| | Na (D line). | Hg (yellow). (green). | Hg(green)/ Na(yellow). | Hg(yellow)/ Na(yellow). |
| <i>d</i> -Base ion | +673.6° | +705.5° | 1.193 | 1.047 |
| <i>d</i> -Acid ion | +18.4 | +54.0 | 1.435 | 1.163 |

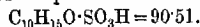
Consideration of the above table indicates that the discrepancies between the rotatory dispersions of the two pairs of enantiomorphously related salts are due to the existence of considerable differences between the rotatory dispersions of the basic and acidic ions produced from the salts in aqueous solution. Whilst the optical behaviour of the salts in question is up to this point entirely in accordance with what would be expected, it is at least remarkable that the molecular rotatory power of the acidic ion is considerably smaller than the value hitherto accepted; the examination of the ammonium salt of *d*-camphor- β -sulphonic acid and of the salts which the latter forms with *d*- and *l*-tetrahydroquinidine (Pope and Peachey, Trans., 1899, 75, 1085) leads to the conclusion that the acidic ion has the molecular rotatory power $[M]_D + 51.7^\circ$, whilst the results stated above indicate that the value should be taken as $[M]_D + 46.4^\circ$. It thus seemed important to obtain further experimental data to supplement the small amount of information now available concerning the rotatory powers of the *d*-camphor- β -sulphates, and Mr. P. V. Delahunty, M.Sc.Tech., has examined carefully purified samples of a number of such salts and of the parent acid; the results of his determinations are now given.

d-Camphor- β -sulphonic Acid.

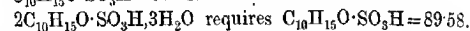
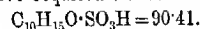
This acid was prepared by the method described by. Reychler (*Bull. Soc. chim.*, 1898, [iii], 19, 120), and, after separation from

the acetic acid solution, was recrystallised repeatedly from ethyl acetate; during the crystallisation it was several times exposed over alkali hydroxide in a vacuum to free it from acetic acid, which it retains with some tenacity. Solutions of the purified acid dissolve magnesium freely in the cold and zinc on slight warming, but do not act on copper at the boiling point; the crystalline acid was subsequently exposed to the air, and the following determinations made with two separate preparations:

1.0012 required 0.15624 Na·OH for neutralisation.



2.1170 required 0.33006 Na·OH for neutralisation.



The above sample of the acid, which thus contains 90.45 per cent. of camphorsulphonic acid, gave the following results on determination of rotatory power in aqueous solution in 2-dm. tubes at 16°:

| Weight in 25 c.c. | α_D | $[\alpha]_D$ | $[\text{M}]_D$ |
|--------------------|------------|--------------|----------------|
| 1.1713 grams | +1.82° | +21.44° | +49.7° |
| 1.0430 „ | +1.65 | +21.86 | +50.7 |
| 1.0431 „ | +1.83 | +21.59 | +50.1 |

The mean molecular rotatory power in the dilute aqueous solution is thus $[\text{M}]_D + 50.2^\circ$.

Ammonium d-Camphor-β-sulphonate.

This salt was prepared in the usual manner, and was obtained as a mass of white needles; three separate preparations indicated, on distillation with soda and titration with acid, the presence of 7.59, 7.69, and 7.64 per cent. of ammonium, NH_4 , respectively, in place of the theoretical percentage of 7.23. The cause of this slight discrepancy was not traced. The following determinations were made in aqueous solutions at 16°, 2-dm. tubes being used:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[\text{M}]_D$ |
|------------------|------------|--------------|----------------|
| 1.1726 | +1.92° | +20.46° | +50.9° |
| 1.0536 | 1.72 | 20.40 | 50.8 |
| 1.1295 | 1.85 | 20.47 | 50.8 |

The mean molecular rotatory power in dilute aqueous solution is thus $[\text{M}]_D + 50.8^\circ$.

Potassium d-Camphor-β-sulphonate.

This salt was prepared in the usual manner, and when purified by crystallisation from alcohol, is obtained in colourless needles, which contain no solvent of crystallisation:

0.7860 gave 0.7150 K_2PtCl_6 . $K=14.60$.

$C_{10}H_{15}O_4SK$ requires $K=14.44$ per cent.

The following determinations of rotatory power were made in aqueous solutions at 16° in 2-dcm. tubes:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[M]_D$ |
|------------------|------------|--------------|---------|
| 1.1180 | +1.64° | +18.32° | +49.5° |
| 1.0656 | 1.81 | 18.37 | 49.6 |
| 1.0910 | 1.60 | 18.33 | 49.5 |

Calcium d-Camphor- β -sulphonate.

On treating a solution of the acid with lime, precipitating the excess of the latter with carbon dioxide, filtering, and concentrating, the calcium salt is obtained in large, colourless prisms:

1.0685 gave 0.2540 $CaSO_4$. $Ca=6.99$.

2.0298 lost 0.2613 at 105° . $H_2O=12.87$.

$(C_{10}H_{15}O_4S)_2Ca \cdot 4H_2O$ requires $Ca=6.97$; $H_2O=12.54$ per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[M]_D$ |
|------------------|------------|--------------|---------|
| 1.0042 | +1.39° | +17.30° | +49.6° |
| 1.0151 | 1.40 | 17.18 | 49.3 |
| 1.2048 | 1.65 | 17.12 | 49.1 |

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D + 49.3^\circ$.

Barium d-Camphor- β -sulphonate, $(C_{10}H_{15}O_4SO_3)_2Ba \cdot 3H_2O$.

This salt was prepared by treating the ammonium salt with arya, separating the excess of the latter in the usual way, and concentrating the filtered solution until crystallisation occurred; it was purified by recrystallisation from water, and finally obtained in colourless needles. The solvent of crystallisation is only lost completely at $120-130^\circ$, and the anhydrous salt is hygroscopic:

1.0124 gave 0.3600 $BaSO_4$. $Ba=20.90$.

1.7860 lost 0.1473 at 130° . $H_2O=8.25$.

$(C_{10}H_{15}O_4S)_2Ba \cdot 3H_2O$ requires $Ba=20.98$; $H_2O=8.27$ per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[M]_D$ |
|------------------|------------|--------------|---------|
| 1.1760 | +1.43° | +15.30° | +49.6° |
| 1.0186 | 1.23 | 15.18 | 49.5 |
| 1.0422 | 1.27 | 15.23 | 49.7 |

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D + 49.6^\circ$.

Zinc d-Camphor-β-sulphonate, (C₁₀H₁₅O₄S)₂Zn, 6H₂O.

The zinc salt, prepared by double decomposition between the barium salt and zinc sulphate, crystallises in lustrous, six-sided prisms, which melt at 167°.

0.9052 lost 0.1540 at 130°. H₂O = 17.01.

1.0136 gave 0.1300 ZnO. Zn = 10.29.

(C₁₀H₁₅O₄S)₂Zn, 6H₂O requires H₂O = 17.01; Zn = 10.33 per cent.

The following determinations were made in aqueous solutions at 16° in 2-dm. tubes:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[M]_D$ |
|------------------|------------|--------------|---------|
| 1.0001 | +1.24° | +15.49° | +49.2° |
| 1.0130 | 1.26 | 15.55 | 49.1 |
| 1.0132 | 1.25 | 15.42 | 49.0 |

The mean molecular rotatory power in aqueous solution is thus $[M]_D + 49.2^\circ$.

Silver d-Camphor-β-sulphonate, C₁₀H₁₅O·SO₃Ag.

This salt, prepared by dissolving silver hydroxide in the aqueous acid, crystallises in colourless needles, and is readily soluble in water and alcohol:

1.0506 gave 0.4466 AgCl. Ag = 31.97.

C₁₀H₁₅O₄SAg requires Ag = 31.86 per cent.

The following determinations were made in aqueous solutions at 16° in 2-dm. tubes:

| Grams in 25 c.c. | α_D | $[\alpha]_D$ | $[M]_D$ |
|------------------|------------|--------------|---------|
| 1.0010 | +1.17° | +14.61° | +49.5° |
| 1.0730 | 1.25 | 14.56 | 49.1 |
| 1.1008 | 1.23 | 14.54 | 49.2 |

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D + 49.4^\circ$.

In addition to the salts described above, the cupric salt, crystallising with 5.5 molecules of water in pale blue rhombs, and the ferric salt, crystallising in yellowish-green leaflets, have also been prepared.

It is noteworthy that in the concentrations used, all the above compounds, with the exception of the free acid and its ammonium salt, give molecular rotatory powers less than $[M]_D + 50^\circ$; this value is notably less than was obtained by Pope and Peachey from examination of the ammonium salt. The still smaller value of $[M]_D + 46.4^\circ$ obtained for the acidic ion by the examination of the pavine salts described above possibly result from the greater degree of molecular dilution in which the latter salts were examined; in

this connexion. it is worthy of note that Walden (*Zeitsch. physikal. Chem.*, 1891, 15, 196) found that the molecular rotatory powers of the *d*- α -bromocamphor- π -sulphonates decreased slightly as the dilution increased in aqueous solution.

d- and l-Pavine d-Tartrates.

Since externally compensated pavine cannot be resolved by crystallisation with *d*-tartaric acid, owing to the formation of a well-characterised partly racemic *dl*-pavine *d*-tartrate (Goldschmiedt, *Monatsh.*, 1898, 19, 321; Pope and Peachey, *Trans.*, 1898, 73, 902), it appeared of interest to prepare and examine the *d*-tartrates of both *d*- and *l*-pavine. The salts were prepared by dissolving equivalent quantities of the base and acid in aqueous alcohol and evaporating to dryness; the partly crystalline residues were then dissolved in dry acetone and precipitated as microcrystalline, white powders by the gradual addition of dry ether. Both salts absorb moisture from the air, and are extremely soluble in water and most organic solvents; they thus contrast strongly with *dl*-pavine *d*-tartrate, which is stable in the air, and dissolves sparingly in water and alcohol.

d-Pavine d-Tartrate, $2C_{20}H_{23}O_4N_2C_4H_6O_6 \cdot 6H_2O$.

This salt readily absorbs moisture after drying in a vacuum desiccator, and, for purposes of analysis, was exposed to the air until constant in weight:

0.1170 gave 0.2401 CO_2 and 0.0682 H_2O . $C = 55.97$; $H = 6.52$.

0.4304 lost 0.0394 at 105° . $H_2O = 9.03$.

$C_{44}H_{54}O_{20}N_4$ requires $C = 56.14$; $H = 6.86$; $H_2O = 11.50$ per cent.

An accurate determination of the water of crystallisation could not be made, because decomposition sets in before the salt becomes anhydrous; the above analyses merely show that the salt is the normal tartrate. It melts and decomposes at $156-158^\circ$:

0.2260 gram, dried at 105° , and made up to 20.0 c.c. with water at 22° , gave $\alpha_D + 3.56^\circ$ in a 2-dm. tube, whence $[\alpha]_D + 157.5^\circ$.

l-Pavine d-Tartrate, $2C_{20}H_{23}O_4N_2C_4H_6O_6 \cdot H_2O$.

After drying at 105° , this salt was found by the following analyses to retain one molecule of water of crystallisation; like the corresponding salt of *d*-pavine, it melts and decomposes at $156-158^\circ$:

0.1658 gave 0.3759 CO₂ and 0.0950 H₂O. C=61.81; H=6.40.

0.1694 „ 0.3862 CO₂ „ 0.0968 H₂O. C=62.16; H=6.39.

C₄₄H₅₄O₁₅N₂ requires C=62.10; H=6.40 per cent.

0.2810 gram, made up to 20.0 c.c. with water at 22°, gave α_D -4.23° in a 2-dm. tube, whence [α]_D -150.5°.

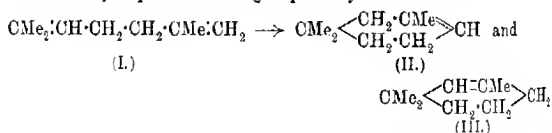
UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCXXXI.—*Synthesis of 1:1:3-Trimethylcyclohexene (cycloGeraniolene).*

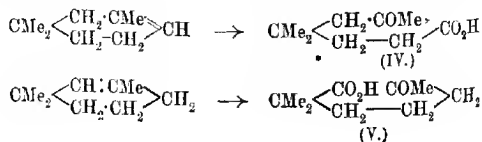
By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING (Salters' Fellow).

SOME years ago Tiemann and Semmler (*Ber.*, 1893, **26**, 2708) prepared from the aldehyde citral (geranial) an open-chain hydrocarbon, C₉H₁₆, named by them geraniolene. The constitution of this substance (I) follows from that of citral, which was established by Barbier and Bouveault in 1896 (*Compt. rend.*, **122**, 393).

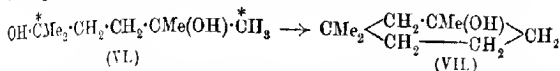
When geraniolene is shaken with a 60 per cent. solution of sulphuric acid, an isomeric change takes place, the open-chain hydrocarbon being converted into a mixture of two cyclic hydrocarbons, α- and β-cyclogeraniolene (II and III), in which mixture the α-variety is present in larger quantity:



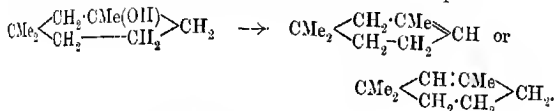
The constitutional formulæ of these hydrocarbons were ultimately determined by Tiemann (*Ber.*, 1898, **31**, 816, 881; 1900, **33**, 3711) from a study of their oxidation with potassium permanganate, the products isolated being two ketonic acids, isogeronic (IV) and geronic (V) acids, together with α-dimethylsuccinic acid and ββ-dimethylglutaric acid.



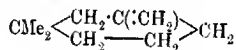
The formation of the two modifications of *cyclogeraniolene* was ascribed to the addition of two molecules of water to the molecule of geraniolene which were subsequently eliminated. According to Tiemann, hydroxyl groups became attached to the carbon atoms bearing methyl groups, so that the first stage in the reaction consists in the formation of a compound of formula VI; this is succeeded by ring-formation due to elimination of a molecule of water and subsequent union of the two carbon atoms marked *:



It is obvious that the second molecule of water may be eliminated from the compound (VII) in two different ways, and the formation of the two modifications of *cyclogeraniolene* is thus explained:



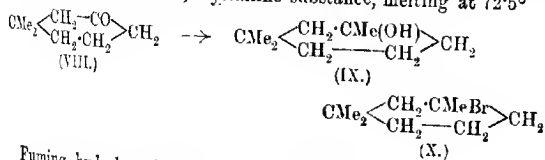
A third hydrocarbon having the formula:



is a possibility, but no evidence of its presence is recorded.

Tiemann did not actually isolate either of the hydroxy-compounds VI or VII, but a synthesis of 1:1:3-trimethylcyclohexan-3-ol (VII) has now been effected by a method which leaves no doubt as to its constitution, and it is found that this alcohol can be readily converted into *cyclogeraniolene*, thus affording confirmation of Tiemann's supposition.

The starting point was 1:1-dimethylcyclohexan-3-one (VIII), prepared by the action of reducing agents on 5-chloro-1:1-dimethylcyclohexan-3-one (Trans., 1907, 91, 81). When this ketone is treated with an ethereal solution of magnesium methyl iodide and the product decomposed with water, trimethylcyclohexanol (IX) is obtained as a well-defined, crystalline substance, melting at 72.5°

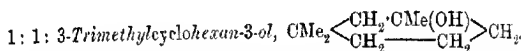


Fuming hydrobromic acid converts the alcohol into 3-bromo-1:1:3-trimethylcyclohexane (X), which, when treated with alcoholic potassium hydroxide, loses the elements of hydrogen

bromide in two ways, giving rise to the same mixture of hydrocarbons as described by Tiemann.

The work of Tiemann on the preparation of *cyclogeraniolene* was repeated by Wallach (*Annalen*, 1902, **324**, 97), who prepared the nitrosate of α -*cyclogeraniolene*, and proved that it was transformed by the action of alkalis into the oxime of 1:1:3-trimethyl- Δ^2 -cyclohexen-4-one. The identity of the hydrocarbons described in the present communication with *cyclogeraniolene* has been established by preparing this crystalline nitrosate, and from it the above-mentioned oxime; further, by oxidising the hydrocarbons with potassium permanganate, when the products isolated were *as*-dimethylsuccinic acid, *isogeronic* and *geronic* acids, the two latter being identified as their semicarbazones, melting at 195° and 164° respectively.

EXPERIMENTAL.



Thirty grams of 1:1-dimethylcyclohexan-3-one (Trans., 1907, **91**, 81), dissolved in an equal volume of ether, were gradually added to a Grignard reagent prepared from 33 grams of methyl iodide and 5.7 grams of magnesium turnings in 100 c.c. of dry ether. The ethereal solution was gently boiled on a water-bath for one hour, cooled, and poured into a concentrated solution of ammonium chloride, to which ice had been added. The ethereal layer was separated, the saline solution extracted three times with ether, the mixed ethereal liquids washed, dried over potassium carbonate, and evaporated, when a solid residue (23 grams = 70 per cent. of the theoretical amount) was obtained, which, after drying on porous plate, was recrystallised from dilute alcohol and analysed:

0.1061 gave 0.2965 CO_2 and 0.1209 H_2O . C = 76.21; H = 12.66.

$\text{C}_9\text{H}_{18}\text{O}$ requires C = 76.06; H = 12.67 per cent.

1:1:3-Trimethylcyclohexan-3-ol is readily soluble in the cold in all the ordinary organic solvents, and may be crystallised from dilute alcohol or dilute acetone, from which it separates in beautiful four-sided, elongated prisms, having a characteristic, strongly camphoraceous odour, and melting at 72.5°.

3-Bromo-1:1:3-trimethylcyclohexane.

Trimethylcyclohexanol, in quantities of 10 grams at one time, were sealed up with 50 c.c. of a solution of hydrogen bromide (saturated at 0°) in small soda-water bottles, which were heated in a boiling-water bath for one hour. The mixture was poured

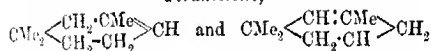
into water, extracted three times with ether, the ethereal solution washed with a solution of sodium hydrogen carbonate, then with water, dried, evaporated, and the residue distilled under diminished pressure, when, after two distillations, 11.5 grams passed over constantly at $88^{\circ}/20$ mm.:

0.1527 gave 0.1375 AgBr. Br=38.31.

$C_9H_{17}Br$ requires Br=39.02 per cent.

Bromotrimethylcyclohexane is, when freshly prepared, a faintly yellow liquid boiling at $88^{\circ}/20$ mm., which, especially on exposure to air, evolves fumes of hydrogen bromide and rapidly decomposes, becoming green, and finally black. The rapidity with which this decomposition takes place accounts, no doubt, for the low result for bromine quoted above.

1:1:3 Trimethyl- Δ^3 - and - Δ^2 -cyclohexenes. α - and β -cyclo-Geraniolene,



Thirty grams of potassium hydroxide were dissolved in a little water, and added to 35 grams of bromotrimethylcyclohexane dissolved in 150 c.c. of absolute alcohol. The whole was heated on the water-bath for one hour, cooled, poured into water, and extracted four times with ether; the ethereal solution was washed, dried, and evaporated, and the residue distilled, when the following fractions were collected: $110-136^{\circ}=2$ grams; $136-142^{\circ}=13$ grams; $142-150^{\circ}=3$ grams. The fraction $136-142^{\circ}$ was twice redistilled over sodium and analysed:

0.1244 gave 0.3971 CO_2 and 0.1430 H_2O . C=87.06; H=12.77.

C_9H_{16} requires C=87.10; H=12.90 per cent.

Trimethylcyclohexene (cyclogeraniolene) is a colourless, refractive liquid, possessing a pronounced terpene-like odour. It boils at $137-140^{\circ}/760$ mm., and has a density of 0.8085 at $15^{\circ}/15^{\circ}$.

This hydrocarbon has also been prepared by the action of dehydrating agents on trimethylcyclohexanol (potassium hydrogen sulphate at $130-140^{\circ}$, and zinc chloride at $160-170^{\circ}$) and by shaking trimethylcyclohexanol with dilute sulphuric acid (D 1.67) for several hours at the laboratory temperature. If this latter action is prolonged for several days, the principal product is a polymeric modification of the hydrocarbon boiling at $165-170^{\circ}/30$ mm.

When dissolved in glacial acetic acid and treated with amyl nitrite and nitric acid according to the directions of Wallach

(*loc. cit.*), the mixture of trimethylcyclohexenes, prepared by any of these methods, yielded the crystalline nitrosate of 1:1:3-trimethyl- Δ^3 -cyclohexene, melting at 103–104°, which by the action of sodium methoxide was transformed into the oxime of 1:1:3-trimethyl- Δ^2 -cyclohexen-4-one, melting at 128°.

The hydrocarbon was oxidised with potassium permanganate as described by Tiemann (*Ber.*, 1900, 33, 3711), when the residue obtained on working up the product partly solidified on keeping. It was spread on plate, and the residue crystallised from water, when it melted at 140°. The identity of this substance with *as*-dimethylsuccinic acid was proved by the mixed melting-point method, and by preparing from it an anilic acid, which melted at 186°.

The porous plate (see above), on extraction with ether, yielded an oil which was dissolved in alcohol and treated with a solution of semicarbazido acetate. After some time a solid was deposited, melting at 185–192°, which crystallised from alcohol, in which solvent it is only sparingly soluble, in feathery needles, melting and decomposing at 198°. (Found, N=18.46. $C_{10}H_{16}O_3N_3$ requires N=18.34 per cent.) These data prove the substance to be the semicarbazone of isogeronic acid.

On concentrating the mother liquor from the above semicarbazone, a further quantity of crystals was obtained in glistening lamellæ, melting, after recrystallisation, at 163°. (Found, N=18.37. $C_{10}H_{16}O_3N_3$ requires N=18.34 per cent.) The substance was therefore the semicarbazone of geronic acid (compare Tiemann).

It appeared to be of interest, in connexion with other work which is in hand, to try the action of Grignard reagents, other than magnesium methyl bromide, on dimethylcyclohexanone, but the results are most disappointing, as with increase in the molecular weight of the alkyl group, the yields of the products decrease rapidly, and further work in this direction has been abandoned for the present.

1:1-Dimethyl-3-ethylcyclohexan-3-ol, prepared by the action of magnesium ethyl bromide on 1:1-dimethylcyclohexan-3-one, is a colourless, refractive liquid, boiling at 94°/30 mm., and possessing a penetrating, camphoraceous odour:

0.1363 gave 0.3851 CO_2 and 0.1552 H_2O . C=77.05; H=12.65.

$C_{10}H_{20}O$ requires C=76.93; H=12.82 per cent.

The alcohol is readily converted by the action of fuming hydrobromic acid into 3-bromo-1:1-dimethyl-3-ethylcyclohexane (b. p. 105–106°/22 mm.), from which substance hydrogen bromide is eliminated by potassium hydroxide to give a mixture of isomeric 1:1-dimethyl-3-ethylcyclohexenes:

0.1210 gave 0.3848 CO_2 and 0.1425 H_2O . $\text{C}=86.73$; $\text{H}=13.09$.

$\text{C}_{10}\text{H}_{18}$ requires $\text{C}=86.95$; $\text{H}=13.04$ per cent.

Dimethylethylcyclohexene is a colourless, refractive liquid, boiling at $156^\circ/760$ mm.

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CCXXXII.—*The Constituents of Gelsemium.*

By CHARLES WATSON MOORE.

UNDER the title of "gelsemium" several of the pharmacopœias recognise the dried rhizome and roots of *Gelsemium sempervirens*, Aiton, commonly known as the "yellow jessamine."

The medicinal value of the plant is due to the presence of certain alkaloids, only one of which, however, has been obtained in a crystalline condition.

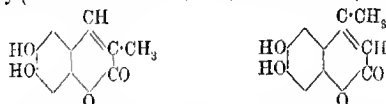
Among the earlier investigations of gelsemium there may be noted that of Wormley (*Amer. J. Pharm.*, 1870, 42, 1), who isolated an impure alkaloidal product to which he gave the name of "gelseminine." This base was afterwards investigated by Sonnenschein (*Ber.*, 1876, 9, 1182) and Gerrard (*Pharm. J.*, 1883, 13, [iii], 641), who assigned to it the formulæ $\text{C}_{22}\text{H}_{28}\text{O}_4\text{N}_2$ and $\text{C}_{24}\text{H}_{28}\text{O}_4\text{N}_2$ respectively. The last-mentioned investigator was the first to obtain gelsemine and its salts in a crystalline state. Thompson (*Jahresber.*, 1887, 2218), who ascribed to gelsemine the formula $\text{C}_{34}\text{H}_{69}\text{O}_{12}\text{N}_4$, showed that it was accompanied in the plant by a second alkaloid, which he obtained in an amorphous condition, and which he designated as "gelseminine." Both gelsemine and gelseminine have more recently been examined by Cushny (*Ber.*, 1893, 26, 1725), who proposed the formulæ $\text{C}_{40}\text{H}_{63}\text{O}_{14}\text{N}_5$ and $\text{C}_{42}\text{H}_{67}\text{O}_{14}\text{N}_5$ respectively for the two bases. Spiegel (*Ber.*, 1893, 26, 1045) suggested the formula $\text{C}_{22}\text{H}_{26}\text{O}_3\text{N}_2$ for the crystalline base, which was confirmed by Geldner (*Ber. deut. pharm. Ges.*, 1895, 5, 330), who obtained it in colourless crystals, melting at 160° .

Some confusion has arisen as to the nomenclature of the two bases isolated from gelsemium; thus in the English literature the crystalline base is referred to as gelsemine, and the amorphous product as gelseminine, whilst most of the German investigators, for example, Spiegel (*loc. cit.*) and Geldner (*loc. cit.*), use these names in the opposite sense. In this communication the English nomenclature is adhered to.

The present investigation has resulted in the isolation of the alkaloid gelsemine in a pure crystalline condition. The base is found to melt considerably higher than has hitherto been recorded (m. p. 178° , instead

of 160°), and it has been conclusively shown to possess the formula $C_{20}H_{22}O_2N_2$. Besides gelsemine and gelseminine, the presence of a third alkaloidal substance in gelsemium has been established. This substance is weakly basic and amorphous, but possesses strongly toxic properties.

It was shown by Wormley (*loc. cit.*) that gelsemine was accompanied in the plant by an acidic substance, which he called "gelseminic acid," an observation which has been confirmed by the present author. Gelseminic or "gelsemic" acid has been shown by Schmidt (*Arch. Pharm.*, 1898, 236, 236) to be a monomethyl ether of asculetin (4:5-dihydroxycoumarin). Two asculetin monomethyl ethers are known, which have been incorrectly termed α - and β -methylasculetin respectively (compare *Beilstein's Handbuch*, III., 568), the compound from gelsemium having been given by Schmidt the latter designation. It is evident, however, that the names α - and β -methylasculetin can only be correctly applied to substances possessing the following formulae respectively (Pechmann and Kraft, *Ber.*, 1901, 34, 423):



Gelseminic acid is, therefore, asculetin 4-(or-5)monomethyl ether, and it is considered desirable to retain for this substance the name "scopoletin," as proposed by Eykman (*Rec. trav. chim.*, 1884, 3, 171), who first obtained it from the rhizome of *Scopolia japonica*. The fluorescent substance, known as β -methylasculetin, which is contained in the bark of *Prunus serotina* and in jalap (Trans., 1909, 95, 243; *J. Amer. Chem. Soc.*, 1910, 32, 93) would accordingly be more appropriately termed scopoletin.

A summary of the results of the complete investigation of gelsemium, is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the dried rhizome and roots of *Gelsemium sempervirens*, Aiton.

A portion (20 grams) of the crushed drug was extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100° , were obtained:

| | | | |
|--|-----------|---|----------------|
| Petroleum (b. p. $85-90^{\circ}$) extracted | 0.39 gram | = | 1.95 per cent. |
| Ether | 0.16 " | | 0.80 " |
| Chloroform | 0.34 " | | 1.70 " |
| Ethyl acetate | 0.16 " | | 0.80 " |
| Alcohol | 1.63 " | | 8.15 " |

Total 2.68 grams = 13.40

For the purpose of a complete examination, 49.44 kilograms of the ground material were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 9.20 kilograms.

Distillation of the Extract with Steam.

A quantity (2 kilograms) of the above-mentioned extract, representing about 10.75 kilograms of the drug, was mixed with water, and steam passed through the mixture for some hours. The distillate, which amounted to 5 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small quantity of an essential oil was obtained. This was a very pale yellow liquid, and amounted to about 2 grams, being thus equivalent to about 0.019 per cent. of the weight of the drug.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as described above, there remained in the distillation flask a quantity of a brown resin (A) and a dark-coloured aqueous liquid (B). The resin was collected, and repeatedly washed with water until nothing further was removed, the washings being added to the above-mentioned aqueous liquid.

This resin was a brown, viscid solid, and amounted to 412 grams. It was dissolved in alcohol and mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with petroleum (b. p. 33—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin (A).

Isolation of Pentatriacontane, $C_{35}H_{72}$, and Emodin Monomethyl Ether.

The petroleum extract, which formed a brown, semi-liquid mass and amounted to 224 grams, was dissolved in 2 litres of warm ether and the solution kept for some days, when a small quantity of an almost colourless substance separated. This was collected and washed with a little ether, after which it was distilled under diminished pressure. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when it was obtained in small, colourless, glistening leaflets, melting at 75°. (Found, C = 84.9; H = 14.5. Calc., C = 85.4; H = 14.6 per cent.)

This substance was therefore pentatriacontane.

The ethereal liquid, from which the pentatriacontane had been removed as above described, was extracted with successive portions of an aqueous solution of sodium carbonate, and finally washed with

water. The alkaline liquids and washings were united, acidified, and extracted with ether, when 15 grams of a viscid, oily liquid were obtained. On distilling this liquid under diminished pressure, it passed over between 245° and $255^{\circ}/25$ mm., and then became almost solid. It consisted of a mixture of fatty acids, which were examined in connexion with a similar product obtained from the non-acidic portion of the petroleum extract after its hydrolysis.

The ethereal liquid, from which the pontatriacontane and free fatty acids had been removed, as above described, was subsequently shaken with a solution of sodium hydroxide. The alkaline extracts, which had assumed a red colour, were acidified and extracted with ether, when a very small quantity of an orange-yellow substance was obtained. This when crystallised from ethyl acetate formed orange-red prisms, which melted at about 190° , and when mixed with a little emodin monomethyl ether, fusion occurred at the same temperature. The quantity so obtained was too small for analysis, but the substance appeared to be emodin monomethyl ether (m. p. 195°), since on heating for a short time with concentrated sulphuric acid it gave a substance soluble in aqueous sodium carbonate and agreeing in its properties with emodin.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The ethereal liquid which had been extracted with alkalis, as above described, was evaporated, when a quantity of an oily product was obtained. This was hydrolysed by heating with an alcoholic solution of potassium hydroxide, the alcohol removed, water added, and the alkaline liquid extracted with ether. The ethereal solution was washed, dried, and the solvent removed, when a quantity of brown resinous material was obtained. This was extracted with cold absolute alcohol, in which only a small portion dissolved. The alcoholic solution was concentrated, and a little water added, when, on keeping, a substance separated in flat needles, which after recrystallisation from a mixture of dilute alcohol and ethyl acetate formed glistening, flat needles, melting at 136° . The amount of this substance was 1.5 grams:

0.1600, on heating at 110° , lost 0.0072 H_2O . $H_2O = 4.5$.

0.1336* gave 0.4110 CO_2 and 0.1455 H_2O . $C = 83.9$; $H = 12.1$.

$C_{27}H_{46}O, H_2O$ requires $H_2O = 4.5$ per cent.

$C_{27}H_{46}O$ requires $C = 83.9$; $H = 11.9$ per cent.

This substance thus agrees in composition with a phytosterol, and it yielded the colour reaction of that class of compounds. A determination of its rotatory power gave the following result:

* Anhydrous substance.

0.2393, made up to 20 c.c. with chloroform, gave $n_D - 0.58'$ in a 2-dm. tube, whence $[\alpha]_D - 40.4^\circ$.

The *acetyl* derivative, when crystallised from acetic anhydride, separated in needles melting at $125-127^\circ$.

The brown resinous material, from which the phytosterol had been removed by extraction with alcohol, as above described, was thoroughly examined, but nothing definite could be isolated from it. It appeared to consist of a mixture of hydrocarbons.

Identification of the Fatty Acids.

The alkaline aqueous solution of potassium salts, from which the phytosterol had been removed by extraction with ether, as above described, was acidified and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A quantity (10 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 240° and $260^\circ/25$ mm. As these acids distilled within the same range of temperature as those previously obtained, which existed in the drug in the free state, for the purpose of their examination the two portions were mixed.

Twenty grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when a portion dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 11 grams of liquid acids, while the insoluble portion gave 8 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over at about $225^\circ/15$ mm. An analysis and a determination of the iodine value gave the following results:

0.1430 gave 0.4030 CO_2 and 0.1518 H_2O . $\text{C} = 76.8$; $\text{H} = 11.8$.

0.4224 absorbed 0.6783 iodine. Iodine value = 160.

$\text{C}_{17}\text{H}_{32}\text{O}_2$ requires $\text{C} = 76.6$; $\text{H} = 12.1$ per cent. Iodine value = 90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ " $\text{C} = 77.1$; $\text{H} = 11.4$ " " " = 181.4.

In order to obtain more definite information respecting the nature of the above mixture, a quantity of it was oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I., p. 360). This resulted in the formation of tetrahydroxystearic acid (m. p. $157-160^\circ$) and a small quantity of dihydroxystearic acid (m. p. $125-127^\circ$). It may thus be concluded that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, the latter in predominating amount.

The Solid Acids.—These acids melted at about 55° , and on analysis gave the following result:

0.1383 gave 0.3842 CO_2 and 0.1590 H_2O . $\text{C} = 75.8$; $\text{H} = 12.7$.

$\text{C}_{16}\text{H}_{32}\text{O}_2$ requires $\text{C} = 75.0$; $\text{H} = 12.5$ per cent.

$\text{C}_{18}\text{H}_{36}\text{O}_2$ " $\text{C} = 76.1$; $\text{H} = 12.7$ "

From this result it would appear that the solid acids consisted of a mixture of palmitic and stearic acids, the latter predominating.

Ethereal Extract of the Resin.

Isolation of Ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$.

This extract was a brown, amorphous mass, and amounted to 10 grams. It was redissolved in about 500 c.c. of warm ether and kept for some days, when a small quantity of an almost colourless, amorphous substance separated. This was collected and crystallised from a mixture of pyridine and dilute alcohol, when it formed microscopic needles, melting at 290° . (Found, $\text{C} = 72.3$; $\text{H} = 10.5$. Calc., $\text{C} = 72.6$; $\text{H} = 10.5$ per cent.)

This substance was thus identified as ipuranol, and when treated with sulphuric acid and acetic anhydride it yielded the colour reaction shown by this compound. From it was also prepared diacetylipuranol, which separated from acetic anhydride in glistening leaflets, melting at 162° .

The ethereal solution from which the ipuranol had been separated, as above described, was examined, but nothing definite was isolated from it.

The chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 35, 36, and 95 grams respectively, and consisted entirely of amorphous products.

Examination of the Aqueous Liquid (B).

Isolation of Scopoletin.

This liquid, as already indicated, represented that portion of the original alcoholic extract of the drug which was soluble in cold water, and from which the previously-described resin (A) had been removed. It was thoroughly extracted with chloroform, these extracts being washed, dried, and the solvent removed. A quantity (about 5 grams) of a crystalline compound was thus obtained, which, after recrystallisation from alcohol, formed long, almost colourless needles, melting at 204° . Its alkaline solution showed a fine blue fluorescence.

0.1430 gave 0.3286 CO_2 and 0.0550 H_2O . $\text{C} = 62.6$; $\text{H} = 4.2$.

$\text{C}_{10}\text{H}_8\text{O}_4$ requires $\text{C} = 62.5$; $\text{H} = 4.2$ per cent.

A methoxyl determination by means of Perkin's modification of the Ziesel method gave the following result:

0.2132 gave 0.2584 AgI. OMe = 16.0.

$C_{10}H_8O_3 \cdot OMe$ requires OMe = 16.1 per cent.

The substance is thus identified as scopoletin, a methyl ether of esculetin.

Its acetyl derivative separates from acetic anhydride in colourless needles, melting at 177°.

Dibromoscopoletin, $C_{10}H_6O_4Br_2$.—Five grams (six atoms) of bromine were added to a solution of scopoletin (2 grams) in about 50 c.c. of chloroform. Hydrogen bromide was slowly evolved, but the liquid did not become colourless. After keeping some hours, a crystalline substance separated, which was removed and recrystallised from alcohol, when it formed yellow, glistening plates, melting at 249°:

0.1682 gave 0.1800 AgBr. Br = 45.5.

$C_{10}H_6O_4Br_2$ requires Br = 45.7 per cent.

This substance is therefore a *dibromoscopoletin*.

Dibromoscopoletin is sparingly soluble in ether, chloroform, or alcohol, and its solution in alkalis shows a very intense green fluorescence.

The two bromine atoms in dibromoscopoletin appear to be in the benzene nucleus, as this substance instantly decolorises a cold alkaline solution of potassium permanganate, and, therefore, still contains a double linking. In this respect it resembles the dibromocoumarin described by Perkin (Trans., 1870, 23, 371).

On heating dibromoscopoletin with acetic anhydride, it is readily acetylated. The *acetyl* derivative forms colourless prisms, melting at 224°.

Isolation of Gelsemine, $C_{20}H_{22}O_2N_2$.

The aqueous liquid from which the scopoletin had been removed, as above described, was extracted with successive portions of amyl alcohol. This, however, only removed small quantities of an amorphous nitrogenous product, which was non-basic, and from which nothing definite could be isolated. The liquid was accordingly rendered alkaline with sodium carbonate and thoroughly extracted with ether, the combined ethereal extracts being washed, dried, and the solvent removed. A quantity of a pale yellow product was thus obtained, which crystallised very readily from acetone in handsome, glistening prisms, melting at 175–178°. After recrystallisation from the same solvent, its melting point was constant at 178°. The quantity isolated amounted to 12 grams. It gave all the usual reactions characteristic of alkaloids:

1.1448, when heated at 120° , lost 0.1774 acetone. $C_3H_6O = 15.5$.

0.1594* gave 0.4353 CO_2 and 0.0930 H_2O . $C = 74.5$; $H = 6.8$.

0.3458* „ 27.5 c.c. N_2 at 27° and 754 mm. $N = 8.7$.

$C_{20}H_{22}O_2N_2$ requires $C = 74.5$; $H = 6.8$; $N = 8.7$ per cent.

$C_{20}H_{22}O_2N_2 \cdot C_3H_6O$ requires $C_3H_6O = 15.3$ per cent.

This substance, therefore, corresponds with the crystalline alkaloid, gelsemine, which has previously been isolated from gelsemium, and for which, as already mentioned, several empirical formulæ have been suggested. The fact that gelsemine crystallises from acetone with one molecule of this solvent (see above) was confirmed by mixing 1 gram of the air-dried preparation with 20 c.c. of water and distilling the liquid. On adding *p*-bromophenylhydrazine to the distillate, a crystalline precipitate was formed, melting at 93° , which corresponded in all respects with acetone-*p*-bromophenylhydrazone.

The molecular weight of gelsemine was determined by the cryoscopic method in acetic acid solution:

0.5250*, in 24.90 acetic acid, gave $\Delta t = -0.270^{\circ}$. $M.W. = 305$.

$C_{20}H_{22}O_2N_2$ requires $M.W. = 322$.

In benzene solution association occurs, and numbers corresponding with twice this molecular weight are obtained:

0.6340*, in 20.70 benzene, gave $\Delta t = -0.248^{\circ}$. $M.W. = 605$.

$(C_{20}H_{22}O_2N_2)_2$ requires $M.W. = 644$.

In order to ascertain whether gelsemine is homogeneous, a quantity was converted into its hydrochloride, and this salt recrystallised, first from dilute alcohol and then from water. The base was then regenerated, and, after crystallisation from acetone, again analysed:

0.1414* gave 0.3866 CO_2 and 0.0880 H_2O . $C = 74.5$; $H = 6.9$.

$C_{20}H_{22}O_2N_2$ requires $C = 74.5$; $H = 6.8$ per cent.

For further confirmation of the purity of the material, the base was converted into its nitrate. This salt, which forms glistening prisms, melting above 280° , was recrystallised from water, and the base regenerated from it. The product so obtained, after crystallisation from acetone, gave the following results on analysis:

0.1462* gave 0.3980 CO_2 and 0.0906 H_2O . $C = 74.2$; $H = 6.8$.

$C_{20}H_{22}O_2N_2$ requires $C = 74.5$; $H = 6.8$ per cent.

The formula of the base deduced from these analyses is in harmony with the result obtained from the analysis of the hydrochloride.

Gelsemine forms a monohydrochloride crystallising in small prisms, melting indefinitely at about 300° :

0.5614 gave 0.2310 $AgCl$. $Cl = 10.1$.

$C_{20}H_{22}O_2N_2 \cdot HCl$ requires $Cl = 9.9$ per cent.

* Constant at 120° .

A determination of its specific rotatory power gave the following result:

0.3100, made up to 20 c.c. with water, gave $[\alpha]_D + 0.05'$ in a 2-dcm tube, whence $[\alpha]_D + 2.6^\circ$.

The close agreement of these results shows conclusively that the empirical formula of gelsemine is $C_{20}H_{29}O_2N_9$.

A determination of its specific rotatory power gave the following result:

0.4066*, made up to 20 c.c. with chloroform, gave $[\alpha]_D + 0.39'$ in a 2-dcm. tube, whence $[\alpha]_D + 15.9^\circ$.

Examination of the Amorphous Alkaloidal Products.

The alkaline, aqueous liquid from which the gelsemine had been removed by extraction with ether, as above described, was repeatedly extracted by means of amyl alcohol, when a relatively small quantity of an amorphous, basic product was obtained. This appeared to consist of a mixture, and two alkaloidal products were found to be present, one of which was much more strongly basic than the other. It was dissolved in chloroform, and extracted several times with 1 per cent. aqueous hydrochloric acid, which removed the more strongly basic product. The material obtained on rendering the acid extracts alkaline was isolated by means of chloroform, when it formed an amorphous, brown-coloured product. Neither the free base nor any of its salts could be obtained in a crystalline condition. This more strongly basic product appears to correspond with the amorphous alkaloid to which the name "gelseminine" has been given.

The chloroform solution from which the "gelseminine" had been removed by means of 1 per cent. acid, as above described, was shaken many times with 10 per cent. aqueous sulphuric acid, which slowly removed a small quantity of a very weakly basic substance. As in the case of "gelseminine," neither the free base nor its salts could be obtained in a crystalline condition. This substance responds to the usual alkaloid reagents, but appears to be stable only in the form of its salts, as on keeping a chloroform solution of the base for some time the product becomes insoluble in acids.

The alkaline aqueous liquid from which the alkaloidal products had been removed, as above described, was neutralised by means of acetic acid and treated with a solution of basic lead acetate. This produced a voluminous yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture, a liquid was obtained which gave a bluish-black

* Constant at 120° .

coloration with ferric chloride, and evidently contained a quantity of tannin, but no definite products could be isolated from it.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a volume of about 2 litres. The concentrated liquid contained a considerable quantity of a sugar, as it readily reduced Fehling's solution, and yielded *d* phenylglucosazone, melting at 208—210°.

One-fifth of the total liquid was diluted with water to 1 litre, about 50 grams of concentrated sulphuric acid, diluted with an equal weight of water, added, and the liquid repeatedly extracted with chloroform with the object of isolating any organic acids present. As this operation removed only a small quantity of acetic acid, the acid aqueous liquid was boiled for an hour and again extracted with chloroform, when nearly a gram of scopoletin was obtained. It thus appears probable that a glucoside of scopoletin was present in the original aqueous liquid, but all attempts to isolate this substance were unsuccessful.

Physiological Tests.

The following physiological tests were conducted in the Wellcome Physiological Research Laboratories by Dr. H. H. Dale, to whom the author now wishes to express his thanks:

A quantity (0.1 gram) of gelsemine hydrochloride, when injected intravenously into a rabbit, caused practically no effect, a result which is in agreement with an observation by Cushny.

One milligram of the hydrochlorides of both the amorphous bases, when injected intravenously into rabbits, caused death from respiratory failure in about twenty-five minutes, preceded by convulsions.

Summary.

The results of this investigation may be summarised as follows:

The material employed consisted of the dried rhizome and roots of *Gelsemium sempervirens*, Aiton.

An alcoholic extract of the drug, when distilled with steam, yielded a small amount of an essential oil. The non-volatile constituents, as obtained after treating the alcoholic extract with steam, consisted of a brown resin insoluble in water, and material which remained dissolved in the cold aqueous liquid. The resin, amounting to about 3.3 per cent. of the weight of the drug, yielded pentatriacontane; traces of emodin monomethyl ether; a phytosterol, $C_{27}H_{46}O$ (m. p. 133°; $[\alpha]_D -40.4^\circ$); a small amount of ipuranol, $C_{23}H_{38}O_4(OH)_2$; and a mixture of fatty acids, consisting of palmitic, stearic, oleic, and linolic acids. The portion of the alcoholic extract of the drug which was

soluble in water, and from which the above-described resin had been removed, contained scopoletin (a monomethyl ether of æsculetin), which was present in the free state, and also in the form of a glucoside, together with a quantity of sugar. It yielded, furthermore, three alkaloidal products, one of which, gelsemine, has been obtained in a pure crystalline state, melting considerably higher than has hitherto been recorded (178° , instead of 160°), and which has been conclusively shown to possess the formula $C_{20}H_{22}O_2N_2$. The other alkaloidal products, one of which corresponds with the so-called "gelseminine" of Thompson (*loc. cit.*) and Cushny (*loc. cit.*), were amorphous, and no crystalline derivative could be obtained from them.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON.

CCXXXIII.—*The Distillation of Mixtures of Enantiomorphously Related Substances.*

By WILLIAM CHARLES EVANS.

ALTHOUGH most of the possible types of behaviour which can arise during the distillation of mixtures have been experimentally studied, one of the simplest appears hitherto to have escaped investigation. This type is the one in which the two components of the liquid mixture have the same boiling point under all the pressures dealt with, and in which the boiling points of mixtures of all compositions are identical with those of the components under the same pressure. Under these conditions it would be expected that all mixtures of the two components should behave on distillation like a single substance; the composition of the vapour should be the same as that of the liquid even when the pressure is varied, and no separation by fractional distillation should be possible.

Probably the only instances in which conditions of this highly specialised character can be experimentally realised are to be found amongst mixtures of enantiomorphously related substances, and in the study of such cases the delicate nature of the method available for determining the composition of the mixtures greatly facilitates the practical examination. It is, of course, well known that no separation of the optically active components of an externally compensated substance can be effected by fractional distillation; but it has not previously been shown and is not immediately evident

that mixtures of two enantiomorphously related isomerides in any casual proportion would resist separation by fractional distillation. The following observations of the behaviour of optically active mixtures of *d*- and *l*-camphor and also of *d*- and *l*-tetrahydroquinoline were made at the suggestion of Professor Pope for the purpose of obtaining the lacking experimental data.

A. Distillation of Mixtures of d- and l-Camphor.

The mixtures were prepared from natural *d*-camphor and artificially prepared externally compensated camphor in suitable proportions. In the following series of experiments, the camphor was distilled from a retort heated by a naked flame, care being taken to prevent the distillate from solidifying in the neck of the retort; the distillate was collected in a number of fractions, and the specific rotatory power of each determined in benzene solution.

(1) *d*-Camphor alone was distilled, and the specific rotatory powers of the first and last fractions of the distillate, in 10 per cent. solutions, found to be $[\alpha]_D +40.85^\circ$ and $+40.95^\circ$ respectively; these values are identical within the limits of experimental error.

(2) On distilling externally compensated camphor in the same manner, the first and last fractions were found to be optically inactive.

(3) A mixture consisting approximately of one part of *l*-camphor and two parts of *d*-camphor was separated into five fractions by distillation as above described under atmospheric pressure; the specific rotatory powers of the five fractions in 8 per cent. benzene solution were $[\alpha]_D +27.15^\circ$, $+27.02^\circ$, $+27.37^\circ$, $+26.66^\circ$, and $+26.14^\circ$ respectively. A similar distillation was performed with another mixture, and yielded five fractions with the specific rotatory powers $[\alpha]_D +21.40^\circ$, $+20.09^\circ$, $+19.75^\circ$, $+20.21^\circ$, and $+20.03^\circ$ respectively. It will be noted that the rotatory powers of the five fractions composing either series are not identical within the limits of experimental error, so that some slight degree of separation is indicated. In these determinations, however, no special precautions were taken to ensure thorough admixture of the two components before distillation; it therefore seemed possible that, owing to the readiness with which camphor sublimates, the two components, present in the solid state in different quantities, might have sublimed at different rates determined by the surface exposed and the temperature attained by the solid.

(4) The contingency just indicated was obviated by melting together the mixtures of *d*- and *l*-camphor before introducing them into the retort; after taking this precaution, one mixture, similar to those examined in (3), gave five fractions, of which the specific

rotatory powers in 8 per cent. solutions were $[\alpha]_D +20.24^\circ$, $+20.56^\circ$, $+20.55^\circ$, $+20.60^\circ$, and $+20.56^\circ$ respectively. These five values are identical within the limits of experimental error, and it is thus indicated that intimate mixtures of *d*- and *l*-camphor cannot be altered in composition by distillation under atmospheric pressure.

B. Distillation of Mixtures of d- and l-Camphor in Steam.

(5) A mixture prepared from *d*-camphor and externally compensated camphor, and consisting of about two parts of *d*-camphor and one of *l*-camphor, was distilled in a current of steam, three fractions being collected; these, and the residue left in the distilling flask, were collected and dried in the air. The three fractions and the residue gave the specific rotatory powers, in 4 per cent. benzene solution, of $[\alpha]_D +16.44^\circ$, $+15.24^\circ$, $+14.55^\circ$, and $+27.90^\circ$ respectively; repetition of the operation with another similar mixture yielded four fractions and a residue, which gave the specific rotatory powers of $[\alpha]_D +15.95^\circ$, $+14.28^\circ$, $+14.15^\circ$, $+14.49^\circ$, and $+27.15^\circ$ respectively. No precautions were taken to ensure intimate admixture of the *d*- and *dl*-camphor previous to the steam distillation, and the variations in the specific rotatory power of the distillate and the large difference between these values and those referring to the residues left in the distilling flask might, it was anticipated, be due to differences in the rate of sublimation in steam of the solid active and externally compensated substances.

(6) That the cause just suggested of the variable rotatory powers of the distillate and residue is the true one was demonstrated by the following trials. A mixture of approximately one part of *d*-camphor and two parts of externally compensated camphor was melted and allowed to solidify, then roughly ground, and subjected to steam distillation as described under (5). The three fractions of camphor which distilled and the residue which remained in the still, examined in 5 per cent. benzene solution, gave the specific rotatory powers $[\alpha]_D +21.54^\circ$, $+21.26^\circ$, $+21.62^\circ$, and $+21.55^\circ$ respectively.

The close approximation to constancy of these numbers shows that mixtures of *d*- and *l*-camphor, if care is taken to ensure intimate admixture, behave like a single substance on distillation in a current of steam.

C. Distillation of Mixtures of d- and l-Tetrahydroquinoline.

As indicated in the previous pages, the investigation of the problem under consideration with the aid of mixtures of *d*- and *l*-camphor is complicated by the fact that these substances are solid at the ordinary temperatures, and that their melting and boiling points do not differ greatly. Further information was therefore

sought from the study of mixtures of *d*- and *l*-tetrahydroquinaldine.

Externally compensated tetrahydroquinaldine was treated with *d*- α -bromocamphor- π -sulphonic acid, and the *l*-component of the base in large measure separated by Pope and Peachey's method (Trans., 1899, 75, 1068); the mixture of the *d*-base with a small proportion of the *l*-isomeride remaining after the separation of the *l*-tetrahydroquinaldine *d*- α -bromocamphorsulphonate was isolated by distilling the mother liquors in a current of steam after addition of lime. Such mixtures were used in the following series of experiments.

(7) Two specimens of the mixed *d*- and *l*-tetrahydroquinaldine, containing (a) about 75 per cent. of *d*- and 25 per cent. of *l*-tetrahydroquinaldine, and (b) about 56 per cent. of *d*- and 44 per cent. of *l*-tetrahydroquinaldine, were distilled from Wurtz flasks under a pressure of 300 mm. of mercury. The rotatory powers, α_D , of the several fractions collected were determined in 100 mm. tubes at 16°:

| Fractions. | (a.) α_D . | (b.) α_D . |
|------------|----------------------|----------------------|
| 1 | +28.39° | +6.85° |
| 2 | 28.47 | 6.87 |
| 3 | 28.48 | 6.87 |
| 4 | 28.46 | 6.89 |
| 5 | 28.41 | 6.87 |
| 6 | 28.44 | 6.88 |
| 7 | 28.43 | 6.87 |
| 8 | 28.47 | |
| 9 | 28.49 | |

(8) Two specimens of the mixed bases containing (c) about 65 per cent. of *d*- and 35 per cent. of *l*-tetrahydroquinaldine, and (d) and (e) about 78 per cent. of *d*- and 22 per cent. of *l*-tetrahydroquinaldine, were distilled from a Wurtz flask over a naked flame, (c) under pressures increased gradually from 55 to 415 mm. of mercury, (d) under atmospheric pressure, and (e) under pressures which were caused to rise and fall during distillation between 140 and 600 mm. of mercury. The rotatory powers observed in 100 mm. tubes of the various fractions collected are stated in the appended table:

| Fractions. | (c.) α_D . | (d.) α_D . | (e.) α_D . |
|------------|----------------------|----------------------|----------------------|
| 1 | +11.34° | +33.42° | +33.40° |
| 2 | 11.39 | 33.43 | 33.38 |
| 3 | 11.40 | 33.46 | 33.39 |
| 4 | 11.38 | 33.45 | 33.45 |
| 5 | 11.40 | 33.42 | 33.39 |
| 6 | 11.38 | 33.46 | 33.45 |
| 7 | 11.39 | | |
| 8 | 11.38 | | |
| 9 | 11.39 | | |
| 10 | 11.39 | | |

From the above results, it is to be concluded that on distilling mixtures of enantiomorphously related compounds under varying conditions of pressure, no difference in composition is to be observed between the various fractions of the distillate by determination of the rotatory powers, and that therefore no separation of such mixtures into their optically active components is possible by distillation. The fact that no change in rotatory power can be detected in partly compensated mixtures of either *d*- and *l*-camphor or *d*- and *l*-tetrahydroquinoline on fractional distillation may doubtless be regarded as a demonstration that under the conditions prevailing during distillation no combination of a racemic character exists between the enantiomorphously related isomerides.

The above are the first recorded instances of the theoretically simplest case arising in the distillation of mixtures, but no doubt such instances could be easily multiplied amongst other mixtures of enantiomorphously related compounds.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE.

(CCXXXIV).—The Tertiary Acidic and Alkyl Derivatives of *d*-Camphorimide.

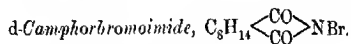
By WILLIAM CHARLES EVANS.

ALTHOUGH it is generally recognised that phthalic acid and camphoric acid exhibit striking analogies in chemical behaviour, the similarities existing between the two acids have not previously been traced in the reactions of their imides. At the suggestion of Professor W. J. Pope, I have therefore endeavoured to ascertain to what extent the reactions by means of which the imidogen hydrogen atom in phthalimide can be replaced by halogen atoms and by alkyl groups are capable of effecting similar substitutions in *d*-camphorimide; that a very deep-rooted analogy in chemical behaviour exists between the two acid imides will be evident from the description of the modes of preparation of the compounds described below.

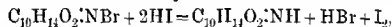
Preparation of d-Camphorimide.

A comparison of the various methods which have been described for the preparation of *d*-camphorimide showed that a method identical in principle with that given by Bredt (*Annalen*, 1903, 328, 344) is the most convenient for use in the preparation of this

substance. *d*-Camphoric acid is gently boiled in a retort provided with a long and wide-necked retort heated in a metal-bath; at the same time a brisk current of dry ammonia gas is passed through the boiling acid from a steel storage cylinder. After the evolution of water vapour has completely ceased, the material is distilled, and, in order to ensure that no camphoric anhydride has escaped conversion, the distillate is once more distilled in a current of ammonia gas. The *d*-camphorimide thus obtained is practically pure, and, after crystallisation from dilute alcohol, melts at 243° .



To a cold solution of 12.3 grams of *d*-camphorimide and 2.7 grams of sodium hydroxide in 125 c.c. of water is gradually added a well-cooled solution of 11 grams of bromine in 250 c.c. of water; a white, crystalline substance immediately separates, which, after collection and crystallisation from benzene, is obtained in minute, white crystals, melting at 154° . The compound thus obtained dissolves readily in chloroform, acetone, ether, or ethyl acetate, and is less soluble in alcohol or benzene. It is decomposed by hydriodic acid in accordance with the equation:



and, in accordance with this reaction, its analysis was effected by dissolving a weighed quantity in chloroform, to which a little potassium iodide and acetic acid had been added, and titrating the liberated iodine with thiosulphate solution:

0.1856 required 15.4 c.c. thiosulphate (1 c.c. = 0.02269 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). Br = 30.36.

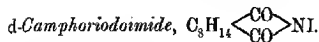
0.1822 gave 0.3086 CO_2 and 0.0930 H_2O . C = 40.20; H = 5.67.

$C_{10}H_{14}O_2 \cdot \text{NBr}$ requires Br = 30.77; C = 40.16; H = 5.39 per cent.

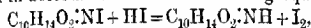
The following determinations of rotatory power were made in 2.2-dm. tubes at 18° :

| Solvent. | Weight in 25 c.c. | α_D . | $[\alpha]_D$. |
|------------------|-------------------|--------------|----------------|
| Benzene | 0.4853 gram | +0.51° | +12.0° |
| " | 0.5960 " | 0.587 | 11.2 |
| " | 0.7797 " | 0.81 | 12.0 |
| Chloroform | 0.4161 " | 0.512 | 13.6 |
| " | 0.6343 " | 0.785 | 13.0 |
| " | 0.7160 " | 1.29 | 12.3 |

The substance is not completely stable in moist air, and to this must be attributed the slight variations in specific rotatory power obvious above.



d-Camphorimide (5 grams, 1 mol.) and sodium hydroxide (1·3 grams, 1 mol.) are dissolved in water (350 c.c.), and the resulting solution added slowly and with vigorous stirring to a well-cooled solution of iodine (3·5 grams, 1 mol.), sodium bromide (5 grams), and bromine (2·3 grams, 1 mol.) in water (50 c.c.). A greyish-black solid immediately separates, which, on stirring, becomes brown; after collection, washing, and drying in a vacuum, the substance is crystallised from hot benzene, from which it separates in minute, light yellow crystals, melting and decomposing at 207°. The iodo-derivative thus obtained is readily soluble in acetone, chloroform, or ether, but less soluble in alcohol or benzene. It reacts with hydriodic acid in accordance with the following equation:



and, in accordance therewith, the iodine was determined by dissolving a weighed quantity in chloroform, adding potassium iodide and acetic acid, and titrating with thiosulphate:

0·2458 required 17·25 c.c. thiosulphate (1 c.c. = 0·02260

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. $\text{I} = 40·76$.

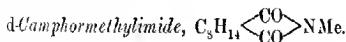
0·1632 gave 0·2330 CO_2 and 0·0717 H_2O . $\text{C} = 38·94$; $\text{H} = 4·88$.

$C_{10}H_{14}O_2\text{NI}$ requires $\text{I} = 41·37$; $\text{C} = 39·09$; $\text{H} = 4·56$ per cent.

The following determinations of rotatory power were made:

| Solvent. | Weight in 25 c.c. | α_D . | $[\alpha]_D$. |
|------------------|-------------------|--------------------------|----------------|
| Chloroform | 0·3852 gram | +0·511° in 2·2-dm. tube. | +15·2° |
| „ | 0·5180 „ | 0·690 „ 2·2 „ | 15·3 |
| „ | 0·6448 „ | 0·406 „ 1 „ | 15·7 |
| „ | 0·7468 „ | 0·470 „ 1 „ | 15·7 |
| Benzene | 0·4055 „ | 0·260 „ 1 „ | 16·0 |
| „ | 0·4383 „ | 0·280 „ 1 „ | 16·0 |

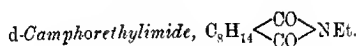
The solutions in chloroform rapidly undergo decomposition and become deep violet in colour.



The method of preparation of this substance described by Hoogewerff and van Dorp (*Rec. trav. chim.*, 1893, 12, 13) may be conveniently replaced by the following simpler one. Camphorimide (5 grams) is dissolved in a mixture of 1·125*N*-potassium hydroxide (27·2 c.c., 1 mol.) and methyl iodide (4 grams); potassium iodide commences to separate in the cold, and the reaction is completed by heating for two hours on the water-bath. After separation of the potassium iodide and evaporation of the alcohol, the residue is dissolved in benzene; the benzene solution, an evaporation, yields

a crystalline residue of *d*-camphormethylimide, which, when crystallised from aqueous alcohol, melts at 46°. Hoogewerff and van Dorp give the melting point as 40–42°. The substance is very soluble in most organic solvents. This compound may be also conveniently isolated from the mixture obtained by heating *d*-camphorimide, potassium hydroxide, and methyl iodide, by treatment with dilute sodium hydroxide solution in order to remove unchanged camphorimide, and crystallising the residue from dilute alcohol. The following determinations of rotatory power were made:

| Solvent. | Weight in 25 c.c. | α_D in 2-dm. tube. | $[\alpha]_D$. |
|---------------|-------------------|---------------------------|----------------|
| Alcohol | 0.6088 gram | +0.54° | +11.1' |
| " | 0.7843 " | 0.69 | 11.0 |
| " | 0.8887 " | 0.81 | 11.4 |
| " | 1.0607 " | 0.96 | 11.3 |
| Acetone | 0.7070 " | 0.45 | 8.0 |
| " | 1.0365 " | 0.685 | 8.0 |



d-Camphorimide (5 grams), 1.125*N*-potassium hydroxide (27.2 c.c.), and ethyl iodide (4.4 grams) were heated together on the water-bath for two hours; after filtration, the alcohol was evaporated off, and the residual sweet-smelling oil washed with dilute sodium hydroxide. The required ethyl derivative remained as an almost colourless solid, which crystallised from dilute alcohol in long, white needles, melting at 51–52°; the following determinations of rotatory power were made:

| Solvent. | Weight in 25 c.c. | α_D in 2-dm. tube. | $[\alpha]_D$. |
|---------------|-------------------|---------------------------|----------------|
| Alcohol..... | 0.5216 gram | +0.52° | +12.4' |
| " | 0.5370 " | 0.54 | 12.6 |
| " | 0.7588 " | 0.76 | 12.5 |
| " | 0.9757 " | 0.955 | 12.6 |
| Acetone | 0.5836 " | 0.395 | 8.4 |
| " | 0.7348 " | 0.52 | 8.8 |
| " | 1.1890 " | 0.81 | 8.5 |

Both the methyl and ethyl derivatives of *d*-camphorimide are practically inactive in benzene solutions.

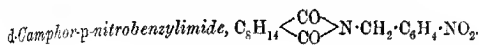
d-Camphorbenzylimide.

This substance was obtained by Hoogewerff and van Dorp (*loc. cit.*) by heating benzylammonium camphorbenzylamate; it is more readily obtained by heating *d*-camphorimide (5 grams) with 1.125*N*-alcoholic potash (27.2 c.c.) and benzyl chloride (3.5 grams) on the water-bath for two hours, evaporating off the alcohol, and adding dilute sodium hydroxide. An almost quantitative yield of the solid product is obtained, which, after crystallisation from dilute

alcohol, melts at 60–62°. The following determinations of rotatory power were made:

| Solvent. | Weight in 25 c.c. | α_D in 2-dem. tube. | $[\alpha]_D$ |
|---------------|-------------------|----------------------------|--------------|
| Alcohol..... | 0.4539 gram | +0.46° | +12.7° |
| " | 0.5776 " | 0.56 | 12.1 |
| " | 0.8032 " | 0.78 | 12.1 |
| Acetone | 0.7067 " | 0.67 | 11.9 |
| " | 0.7388 " | 0.71 | 12.0 |
| " | 0.8361 " | 0.815 | 12.2 |
| " | 0.9848 " | 0.94 | 11.9 |
| Benzene | 0.5476 " | 0.23 | 5.2 |
| " | 0.9557 " | 0.37 | 4.8 |

As in the previous cases the specific rotatory power is much smaller in benzene than in alcohol or acetone solutions.



Camphorimide (5 grams) dissolved in 1.125*N*-alcoholic potash (22.5 c.c.) was heated with *p*-nitrobenzyl chloride (4.75 grams) for a short time on the water-bath; after separating the alcohol and treating with dilute sodium hydroxide, the required derivative was obtained as a yellow solid, which, after crystallisation from alcohol, formed yellow needles, melting at 133°:

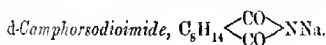
0.1985 gave 0.1709 CO₂ and 0.1142 H₂O. C=64.69; H=6.39.

C₁₇H₂₃O₃N₂ requires C=64.54; H=6.33 per cent.

The following determinations of rotatory power were made:

| Solvent. | Weight in 25 c.c. | α_D in 2-dem. tubes. | $[\alpha]_D$ |
|---------------|-------------------|-----------------------------|--------------|
| Acetone | 0.5071 gram | +0.48° | +11.8° |
| " | 0.6795 " | 0.67 | 12.3 |
| " | 0.7848 " | 0.775 | 12.3 |
| Benzene | 0.5630 " | 0.115 | 2.6 |
| " | 0.9928 " | 0.225 | 2.8 |

The rotatory power has again a smaller value in benzene than in acetone solutions.



This substance separates as a white, flocculent mass on warming a solution of sodium (0.63 gram) in alcohol (2 c.c.) and benzene (5 c.c.), with addition of *d*-camphorimide (5 grams) dissolved in benzene (20 c.c.); after collection and drying in a vacuum, the substance was analysed:

0.6025 gave 0.1990 Na₂SO₄. Na=10.70.

C₁₀H₁₄O₂NNa requires Na=11.33 per cent.

The compound is readily soluble in water or alcohol, and is at once decomposed by acids.

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CCXXXV.—*Azomethineazo-dyes.*

BY ARTHUR GEORGE GREEN and RAJENDRA NATH SEN.

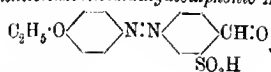
THE azomethine group $\cdot\text{CH}:\text{N}\cdot$ lies between the azo-group $\cdot\text{N}:\text{N}\cdot$ and the stilbene group $\cdot\text{CH}:\text{CH}\cdot$, and in chromophoric power it also occupies an intermediate position. The objects of the present research were twofold, namely, first, to investigate the effect on the colour and dyeing properties of a compound containing both the azomethine and azo-groups, for example, whether such compounds would present similarities to the azostilbene dyes; and secondly, to ascertain how far the presence of auxochromic groups is necessary for the manifestation of dyeing properties in such compounds. In reference to the latter point it may be noted that it has been shown by Green and Crosland (Trans., 1906, 89, 1602) that the dyes of the stilbene class are all azostilbene compounds containing no auxochromic group. Furthermore, dyes which contain no auxochrome are known in some other classes (for example, diamine-gold-yellow).

The method we have employed for preparing azomethineazo-dyes consists in acting on amino-compounds with an azo-aldehyde. As a convenient azo-aldehyde for the purpose, we have selected phenetolenzobenzaldehydesulphonic acid, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{CHO}$, which is readily prepared by oxidation of the dye chrysophenin G with cold aqueous permanganate. By making use of this aldehyde, a number of azomethineazo-dyes have been prepared of varying degrees of complexity, and mostly containing no auxochromic group (unless the ethoxy-group can be considered as such). These are all yellow, crystalline compounds, which dye wool in yellow shades. Although tolerably strong dyes, their colouring power appears somewhat inferior to that of the azostilbene compounds. Affinity for cotton is only slightly developed, except in those cases in which a benzidine or analogous residue is present, and even then it is considerably weaker than in the stilbene series. The introduction of an auxochromic group (OH or NMe_2) has practically no effect on the dyeing properties, and does not increase the tinctorial power, augment the affinity, or change the shade. It is also remarkable that, whilst in the azo-series the introduction of more than one azo-group usually deepens the colour, with these compounds the shade seems almost independent of the number of azomethine groups in the molecule; thus the more complex compounds having two azo-groups and two azomethine groups possess nearly the same colour and tinctorial intensity as those with a single azo-group and a single azomethine group. On the other hand, when dissolved in concentrated sulphuric acid, differences of shade become

apparent: those derived from aniline, aniline-*p*-sulphonic acid, and *p*-aminophenol dissolving with a yellowish red colour, those derived from benzidine and *p*-phenylenediamine with a crimson colour, and those derived from α - or β -naphthylamine with a violet colour. The members of this series which do not contain an auxochromic group possess in common with the dyes of the azostilbene class a considerable degree of fastness to alkalis, chlorine, and light. On the other hand, like other azomethine compounds, they are more or less unstable towards acids which tend to decompose them into the original aldehyde and amine.

EXPERIMENTAL.

Phenetoleazobenzaldehydesulphonic Acid,



This aldehyde was prepared by Green and Meyenberg's method (Eng. Pat. 1431 of 1898). One hundred grams of chrysophenin G cone. (Farbenfabriken vorm. F. Bayer & Co.), which is equivalent to about 22 grams of the pure dye,

$\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4(\text{SO}_3\text{Na}) \cdot \text{CH}=\text{CH} \cdot \text{C}_6\text{H}_4(\text{SO}_3\text{Na}) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$,
were dissolved in 6 litres of boiling water. Into this solution, cooled to 0–5° by addition of ice, was slowly run with rapid mechanical stirring a 3 per cent. solution of potassium permanganate until the colour of the latter was persistent (pale pink filtrate after saturating with sodium chloride). The quantity of permanganate required was 29 grams. After allowing to settle, the supernatant liquor was siphoned off, and the precipitate collected. The solution contained only a small quantity of aldehyde, which was isolated by salting out with potassium or sodium chloride. The main quantity of the aldehyde was contained in the precipitate in admixture with the manganese dioxide. In order to extract it, the precipitate was boiled two or three times with a litre of water, filtered from manganese dioxide, and potassium chloride added to the hot filtrate until precipitation was complete. The potassium salt of the aldehydesulphonic acid thus obtained was collected, washed with 50 per cent. alcohol, and dried. The yield was 81 grams, or 80 per cent. of the theoretical.*

The substance crystallises from water in orange-coloured, microscopic needles, sparingly soluble in cold, but readily so in hot, water. It reacts readily with phenylhydrazine, producing a reddish-orange *phenylhydrazone*. With sodium hydrogen sulphite solution, it gives a yellow,

* The large yield obtained affords incidentally, an additional proof of Richard Meyer's formula for chrysophenin (Ber., 1903, 36, 2970), and definitely establishes the absence of an auxochromic (OH) group in this dye.

crystalline bisulphite compound. In concentrated sulphuric acid it dissolves with a red colour, which on dilution with water becomes yellow. The following results were obtained on analysis:

Found, K = (I) 10.12, (II) 10.18. S = (I) 9.0, (II) 8.9.

$C_{15}H_{13}O_5N_2SK$ requires K = 10.48; S = 8.6 per cent.

An estimation of nitrogen carried out with the barium salt gave:

Found, N = 6.98.

$(C_{15}H_{13}O_5N_2S)_2Ba$ requires N = 6.97 per cent.

A determination of the aldehyde group was effected by titration with a standard solution of phenylhydrazine hydrochloride (containing 1 per cent. of the base) in the presence of sodium acetate, employing *p*-nitrobenzaldehydesulphonic acid as indicator (I). Another method (II) consisted in titrating with a 0.5 per cent. solution of benzidine hydrochloride, but the end point was not very sharp:

Found, CHO = (I) 7.65; (II) 6.73.

$C_{15}H_{13}O_5N_2SK$ requires CHO = 7.8 per cent.

For the preparation of the azomethine dyes, the same general method was employed in all cases. This consisted in mixing in molecular proportions a hot aqueous solution of the potassium salt of the aldehyde with a hot alcoholic or aqueous solution of the respective amine. A few drops of hydrochloric acid were afterwards added, and the mixture was boiled for a few minutes to complete the condensation. The solution was then neutralised with potassium carbonate and left to cool, and the product which separated was recrystallised from dilute alcohol. In some cases (aniline, *p*-nitroaniline, amino-salicylic acid, and *p*-phenylenedimethyldiamine) the amine was dissolved in dilute acetic acid, in which case the condensation completes itself without the addition of hydrochloric acid.

Condensation Product with Aniline: Phenetoleazosulphobenzylideneaniline, $OEt \cdot C_6H_4 \cdot N : N \cdot C_6H_4(SO_3H) \cdot CH : N \cdot C_6H_5$.

The free acid forms an orange-yellow, crystalline precipitate. It dissolves in hot water to an orange-yellow solution, but is almost insoluble in cold water. It dyes wool a fast yellow from a neutral or acetic acid bath, but has no affinity for cotton:

Found, N = 10.39.

$C_{21}H_{19}O_4N_3S$ requires N = 10.27 per cent.

Condensation Product with Aniline-p-sulphonic Acid: Phenetoleazosulphobenzylideneaniline-p-sulphonic Acid,
 $OEt \cdot C_6H_4 \cdot N : N \cdot C_6H_4(SO_3H) \cdot CH : N \cdot C_6H_4 \cdot SO_3H$,

The potassium salt forms fine, reddish-orange needles, fairly soluble

in cold, and readily so in hot, water. It dyes fast yellow shades on wool, but has no affinity for cotton :

Found, $N = 7.58$; $K = 13.44$.

$C_{21}H_{17}O_7N_3S_2K_2$ requires $N = 7.43$; $K = 13.85$ per cent.

Condensation Product with p-Nitroaniline : Phenetoleazosulphobenzylidene-p-nitroaniline, $OEt \cdot C_6H_4 \cdot N : N \cdot C_6H_4(SO_3H) \cdot CH : N \cdot C_6H_4 \cdot NO_2$.

The potassium salt crystallises in bright reddish-orange needles, readily soluble in hot, and fairly so in cold, water. It dyes wool in reddish-yellow shades from a neutral or acetic acid bath, but has no affinity for cotton :

Found, $N = 11.12$; $K = 7.75$.

$C_{24}H_{17}O_6N_4SK$ requires $N = 11.38$; $K = 7.93$ per cent.

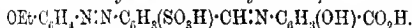
Condensation Product with p-Aminophenol : Phenetoleazosulphobenzylidene-p-aminophenol, $OEt \cdot C_6H_4 \cdot N : N \cdot C_6H_4(SO_3H) \cdot CH : N \cdot C_6H_4 \cdot OH$.

The potassium salt forms fine orange needles, readily soluble in hot water. It dyes wool in reddish-yellow shades, but has no affinity for cotton :

Found, $N = 9.04$; $K = 8.61$.

$C_{24}H_{15}O_6N_3SK$ requires $N = 9.07$; $K = 8.42$ per cent.

Condensation Product with p-Aminosalicylic Acid : Phenetoleazosulphobenzylideneaminosalicylic Acid,

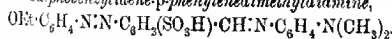


The potassium salt crystallises in orange needles, readily soluble in hot, but sparingly so in cold, water. It dyes wool in reddish-yellow shades fast to alkalis, but only has a small affinity for cotton :

Found, $N = 7.72$; $K = 13.98$.

$C_{22}H_{17}O_7N_3SK_2$ requires $N = 7.70$; $K = 14.31$ per cent.

Condensation Product with p-Phenylenedimethyldiamine : Phenetoleazosulphobenzylidene-p-phenylenedimethyldiamine,



The potassium salt crystallises in water containing potassium carbonate in small leaflets of greenish lustre. It is fairly soluble in cold, and readily so in hot, water. It is easily decomposed by acids. It dyes wool a dull yellow, but has very little affinity for cotton :

Found, $N = 11.16$; $K = 8.26$.

$C_{25}H_{23}O_4N_4SK$ requires $N = 11.43$; $K = 7.96$ per cent.

Condensation Product with α -Naphthylamine: Phenetoleazosulphobenzylidene- α -naphthylamine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{CH} : \text{N} \cdot \text{C}_{10}\text{H}_7$.

The potassium salt forms bright orange, silky needles, sparingly soluble in cold, more readily so in hot, water. It dyes wool reddish-yellow shades from a neutral or acetic acid bath, but has no affinity for cotton:

Found, $\text{N} = 8.51$; $\text{K} = 8.01$.

$\text{C}_{25}\text{H}_{29}\text{O}_4\text{N}_3\text{SK}$ requires $\text{N} = 8.45$; $\text{K} = 7.85$ per cent.

Condensation Product with β -Naphthylamine: Phenetoleazosulphobenzylidene- β -naphthylamine.

The potassium salt forms fine orange needles, readily soluble in hot, but sparingly so in cold, water. It dyes wool reddish yellow shades, but has no affinity for cotton:

Found, $\text{N} = 8.50$; $\text{K} = 7.96$.

$\text{C}_{25}\text{H}_{29}\text{O}_4\text{N}_3\text{SK}$ requires $\text{N} = 8.45$; $\text{K} = 7.85$ per cent.

Condensation Product with Aminoazobenzene: Phenetoleazosulphobenzylideneaminoazobenzene,

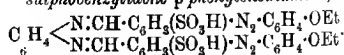
$\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_5$.

The potassium salt crystallises from dilute alcohol in beautiful orange, silky needles. It dissolves in hot water to a yellow solution, but is sparingly soluble in the cold solvent. The addition of hydrochloric acid produces a red precipitate of the free acid. It dyes wool from a neutral or acetic acid bath in yellow shades, which are very fast, to alkalis and light. It also has a moderate affinity for cotton, which it dyes from a salt-bath. The affinity for cotton is, however, considerably less than that of chrysophenin, to which it presents some structural analogy:

Found, $\text{N} = 12.80$; $\text{K} = 6.93$.

$\text{C}_{27}\text{H}_{25}\text{O}_4\text{N}_5\text{SK}$ requires $\text{N} = 12.70$; $\text{K} = 7.07$ per cent.

Condensation Product with p-Phenylenediamine: Bisphenetoleazosulphobenzylidene-p-phenylenediamine,



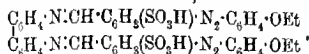
The potassium salt was obtained as a brownish-yellow powder, sparingly soluble in water. It dyes wool in reddish-yellow shades fast

to alkalis and light. It also dyes cotton, for which it has a rather greater affinity than the preceding compound:

Found, N = 9.98; K = 9.52.

$C_{20}H_{16}O_8N_6S_2K_2$ requires N = 10.29; K = 9.59 per cent.

Condensation Product with Benzidine: Bisphenetoleazosulphobenzylidene-benzidine,

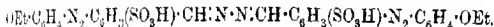


The *potassium* salt forms orange needles, moderately soluble in hot, but sparingly so in cold, water. Hydrochloric acid produces a red precipitate. It dyes wool in fast reddish-yellow shades, and also cotton from a salt-bath in yellow shades tolerably fast to soaping:

Found, N = 9.30; K = 8.99.

$C_{42}H_{34}O_8N_8S_2K_2$ requires N = 9.42; K = 8.75 per cent.

Condensation Product with Hydrazine: Bisphenetoleazobenzaldazine-disulphonic Acid,



This compound was prepared in order to study the tinctorial effect of the double azomethine or aldazine group $\cdot CH : N : N : CH \cdot$. It is obtained by adding 1 gram of hydrazine sulphate dissolved in 20 c.c. of hot water to a solution of 5.7 grams of the aldehyde potassium salt in 300 c.c. of boiling water. The solution, when neutralised with potassium carbonate, deposits the *potassium* salt as a crystalline, yellow precipitate. It crystallises in fine orange needles, sparingly soluble in hot, but almost insoluble in cold, water. Hydrochloric acid produces a red precipitate of the free acid. It dyes wool from a neutral or acetic acid bath in reddish-yellow shades which are fast to alkalis and light. Its affinity for cotton is rather small:

Found, N = 11.22; K = 10.42.

$C_{26}H_{20}O_8N_8S_2K_2$ requires N = 11.35; K = 10.58 per cent.

DEPARTMENT OF TINCTORIAL CHEMISTRY.
UNIVERSITY OF LEEDS.

CCXXXVI.—*Aromatic Hydroxy-sulphoxides.*

By MAUD GAZDAR and SAMUEL SMILES.

In the study of the sulphination of certain phenolic ethers (Smiles and Le Rossignol, *Trans.*, 1908, **93**, 745) several thionyl derivatives of these substances were obtained, and it was found that these methoxy- and ethoxy-sulphoxides when dissolved in concentrated sulphuric acid may be converted by excess of phenolic ether into the triarylsulphonium salts. Later investigation of the corresponding hydroxy-derivatives showed that the reaction is not generally applicable to these substances, for, whilst di-*p*-hydroxyphenyl sulphoxide (Smiles and Bain, *Trans.*, 1907, **91**, 1118) yields the trihydroxyphenyl-sulphonium base, the di-*p*-hydroxy-*m*-tolyl sulphoxide does not (Smiles and Hilditch, *Proc.*, 1907, **23**, 161). The exceptional behaviour of this *p*-cresol sulphoxide is of peculiar interest, for the corresponding dimethyl ether, $(C_6H_3Me \cdot OMe)_2SO$, readily furnishes the triarylsulphonium derivative. Although the so-called "steric" conditions which are set up by substitution in the aromatic nucleus are known to be capable of retarding this reaction (Smiles and Le Rossignol, *loc. cit.*), it cannot be supposed that their influence is the cause of the inactivity of this *p*-cresol sulphoxide. For it is evident from previous experience of "steric hindrance" that, if there be any difference in reactivity between a phenol and its ether, it is the latter that should be less reactive, whereas in the present case the reverse relation holds.

It is a remarkable fact that of the eleven hydroxy- or methoxy-phenyl sulphoxides which have been hitherto examined, all give brilliantly coloured solutions in concentrated sulphuric acid, and it therefore seemed probable that in effecting the condensation of the sulphoxide with the phenolic ether by means of this reagent, some intermediate compound is formed, and that it is the reactivity of this substance that determines the formation of the sulphonium salt.

As a preliminary step in the investigation, we have found it necessary to extend the range of material available, since very little is known of the aromatic hydroxy-sulphoxides, only one, apparently, having been obtained in a pure condition.

The present paper deals with the sulphoxides of *p*-cresol, *p*-chlorophenol, and *o*-chlorophenol. The investigation is not yet complete, but the results are now published, since one of us is unable to carry on the work.

EXPERIMENTAL.

p-Cresol-*m*-sulphoxide, $(OH \cdot C_6H_3Me)_2SO$, (Me:OH:SO=1:4:3.)

The sulphination of *p*-tolyl methyl ether with sulphurous acid and aluminium chloride yields the sulphoxide and a small quantity of

sulphonic acid, the sulphonium base, which is the final product of normal sulphonation, being entirely suppressed (Smiles and Le Rossignol, *loc. cit.*). On applying this method to *p*-cresol, similar products were obtained; but the yields of sulphoxide were poor, hence advantage was taken of the stronger sulphonating power of thionyl chloride. Although this reagent is apt to yield sulphonium salts if allowed to act too energetically, we find that by preserving suitable conditions excellent yields of the sulphoxide are obtained.

Fifteen grams of powdered aluminium chloride were dissolved in an ice-cold solution of 20 grams of *p*-cresol in 50 c.c. of carbon disulphide, and then 20 grams of thionyl chloride were gradually added. The mixture was set aside in a desiccator, and, after the lapse of twenty-four hours, the greater portion of the reaction product—evidently a double salt of the sulphoxide with aluminium chloride—had separated in the form of a yellow, viscous mass. During the next twenty-four hours a further small quantity of this product separated; the supernatant layer of carbon disulphide was then decanted, and the residue decomposed with crushed ice. After being mixed with dilute hydrochloric acid, the mass was treated with a current of steam to remove carbon disulphide and unattacked cresol. After this operation, the contents of the flask were cooled, and the hard, granular mass was collected, dried, powdered, and then extracted with a small quantity of benzene, which removed coloured impurities.

The yield of this product, which consisted of the almost pure sulphoxide, was 20 grams, or about 85 per cent. of the theoretical. It was finally crystallised from hot glacial acetic acid, from which it separated in colourless prisms. The pure substance melts and decomposes at 185°:

0.1706 gave 0.3977 CO_2 and 0.0836 H_2O . $\text{C} = 63.6$; $\text{H} = 5.4$.

$\text{C}_{14}\text{H}_{11}\text{O}_3\text{S}$ requires $\text{C} = 64.12$; $\text{H} = 5.34$ per cent.

It furnishes a bright blue solution with concentrated sulphuric acid, but does not then condense with phenolic ethers, as do other sulphoxides of this group.

Some derivatives of this sulphoxide have been previously investigated by Mr. Hilditch and one of the present authors (*Proc.*, 1907, 23, 161), and, together with others since examined, they are now described in detail.

Dibenzoyl-p-cresol sulphoxide was obtained from the parent substance by the action of benzoyl chloride in alkaline solution. It is soluble in hot alcohol, and separates from that medium in colourless plates, melting at 173°:

0.1375 gave 0.3591 CO_2 and 0.0593 H_2O . $\text{C} = 71.23$; $\text{H} = 4.8$.

$\text{C}_{18}\text{H}_{15}\text{O}_3\text{S}$ requires $\text{C} = 71.46$; $\text{H} = 4.68$ per cent.

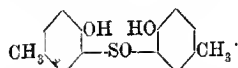
Di-p-cresol Sulphide, (OH·C₆H₃Me)₂S.

The sulphoxide was reduced by the action of zinc dust on the hot solution in glacial acetic acid. On mixing the filtered solution with water, the sulphide separated as a colourless oil, which slowly solidified. After being recrystallised from dilute acetic acid, *di-p-cresol sulphide* was obtained in colourless needles, which melted at 143°:

0.1900 gave 0.4735 CO₂ and 0.0984 H₂O. C = 67.97; H = 5.7.

C₁₄H₁₄O₂S requires C = 68.29; H = 5.68 per cent.

Previous experiments have shown that the sulphoxide which is formed (Smiles and Le Rossignol, *loc. cit.*) by the interaction of thionyl chloride and *p*-tolyl methyl ether contains the quadrivalent sulphur group in the ortho-position with respect to methoxyl, and there can be little doubt that the hydroxy-derivative, which is prepared in a similar manner from *p*-cresol, has the same constitution, namely:



Further and independent evidence in support of this structure will be adduced in a subsequent communication, but at present it may be observed that this is borne out by the behaviour of the substance on nitration. It is extremely easily attacked by nitric acid, two nitro-groups being at first inserted; but attempts to induce further nitration by intensifying the conditions of reaction result in the elimination of the thionyl group with formation of dinitrocresol. The most favourable conditions for nitration are as follows:

Nitric acid (2.7 c.c. of D 1.5) is gradually added to a cooled solution of the sulphoxide (5 grams; about two-thirds of the theoretical amount) in glacial acetic acid (100 c.c.). After three to four minutes a large bulk of water is added. The precipitate is collected and boiled with alcohol to remove soluble impurities, and the insoluble residue finally recrystallised.

Nitro-p-cresol sulphoxide is soluble in hot glacial acetic acid, and very sparingly so in boiling alcohol; it separates from the latter medium in lemon-yellow prisms, which melt at 214°. The scarlet sodium salt is readily soluble in water:

0.1718 gave 0.3009 CO₂ and 0.0545 H₂O. C = 47.7; H = 3.8.

C₁₄H₁₂O₂N₂S requires C = 47.73; H = 3.41 per cent.

Action of Hydrochloric Acid.—Five grams of nitro-*p*-cresol sulphoxide were suspended in about 50 c.c. of alcohol, which had previously been saturated with dry hydrogen chloride at the atmospheric temperature. The mixture was heated to 100° in a sealed tube for four to five

hours. Finally, the solid product was collected, washed with alcohol, and then crystallised from hot glacial acetic acid, from which it separated in long, orange needles. The weight of the crude substance was almost equal to that of the sulphoxide employed. When pure it did not contain halogen:

0.1305 gave 0.2382 CO_2 and 0.0410 H_2O . $\text{C} = 49.78$; $\text{H} = 3.5$.

0.1392 „ 0.2532 CO_2 „ 0.0490 H_2O . $\text{C} = 49.6$; $\text{H} = 3.9$.

$\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_2\text{S}$ requires $\text{C} = 50.00$; $\text{H} = 3.5$ per cent.

The analytical data and the properties of the substance show that it is *nitro-p-cresol sulphide*. This compound melts at 194° , and is soluble in hot alcohol and insoluble in water; the *sodium* salt is deep red in colour. Other sulphoxides, which are described in the following pages, have been treated in a similar manner, and similar reactions have been observed; but with less highly substituted aromatic nuclei chlorination occurs, and even elimination of the sulphur may take place. It may be recalled that other oxygen derivatives of quadrivalent sulphur, namely, the sulphinic acids, are similarly reduced by mineral acids.

p-Chlorophenol Sulphoxide.

The sulphonation of *p*-chlorophenol was effected with thionyl chloride under conditions similar to those described in the preparation of the *p*-cresol derivative. The crude product, which was obtained in a yield of about 70 per cent. of the theoretical, was purified by precipitation with dilute hydrochloric acid from an alcoholic solution. The substance was finally crystallised from dilute alcohol, from which it separated in small, colourless prisms. It melts at 202° , and is sparingly soluble in ether or hot water, and readily so in cold alcohol:

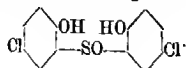
0.1487 gave 0.2580 CO_2 and 0.0366 H_2O . $\text{C} = 47.33$; $\text{H} = 2.73$.

0.3538 „ 0.331 AgCl „ 0.2780 BaSO_4 . $\text{Cl} = 23.2$; $\text{S} = 10.8$.

$\text{C}_{12}\text{H}_9\text{O}_3\text{Cl}_2\text{S}$ requires $\text{C} = 47.52$; $\text{H} = 2.73$; $\text{Cl} = 23.43$;

$\text{S} = 10.56$ per cent.

p-Chlorophenol sulphoxide is soluble in concentrated sulphuric acid, the solution being at first colourless, but rapidly assuming a bright blue colour, which is slowly discharged by the addition of phenetole, indicating the formation of a sulphonium salt. It will be shown in a subsequent communication that the thionyl group in this sulphoxide occupies the *ortho*-position with respect to the two hydroxyl groups of the phenolic nuclei, the substance having the structure:



p-Chloronitrophenol Sulphoxide.

When submitted to the action of nitric acid, this chloro-sulphoxide behaves like the similarly constituted *p*-cresol sulphoxide; two nitro-groups are readily absorbed, but further action of the acid results in decomposition. The dinitro-derivative was prepared in the following manner. The sulphoxide was suspended in about thirty times its weight of cold glacial acetic acid, and while the mixture was stirred, exactly the calculated amount of nitric acid (D 1.42) was added. Stirring was continued until almost all the finely-divided solid had dissolved, then the mixture was rapidly filtered, and the dark reddish-brown filtrates were immediately poured into a large bulk of water. The precipitate was collected and extracted with alcohol; finally, the insoluble portion was recrystallised in small quantities from hot glacial acetic acid. In this way, *p*-chloronitrophenol sulphoxide is obtained in fine yellow needles, which melt at 180—181°. It is insoluble in cold water and sparingly soluble in boiling alcohol:

0.1740 gave 0.2342 CO_2 and 0.0341 H_2O . $\text{C} = 36.7$; $\text{H} = 2.1$.

$\text{C}_{12}\text{H}_6\text{O}_7\text{N}_2\text{Cl}_2\text{S}$ requires $\text{C} = 36.64$; $\text{H} = 1.53$ per cent.

p-Chlorophenol Sulphide.

The sulphide may be obtained by the action of hydrochloric acid on the sulphoxide in alcoholic solution under conditions similar to those described in the preparation of the nitrocresol derivative. To isolate the substance, the mixture was poured into water, and, after some hours had elapsed, the solid was collected and recrystallised several times from benzene, when it was obtained in colourless leaflets which melted at 173—174°. It was found difficult completely to purify this substance, since it tenaciously retained sulphides of higher chlorine content. For comparison, the sulphide was prepared by the reduction of the sulphoxide in the usual manner with zinc dust and boiling acetic acid, and the product, after recrystallisation from benzene, melted sharply at 174° and contained the requisite amount of halogen:

0.1280 gave 0.1288 AgCl . $\text{Cl} = 24.79$.

$\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2\text{S}$ requires $\text{Cl} = 24.71$ per cent.

When mixed with this substance, the product obtained by the former method retained the same melting point.

o-Chlorophenol Sulphoxide.

Sulphination of *o*-chlorophenol was conducted as with *p*-cresol and *p*-chlorophenol; the yield of crude sulphoxide was approximately the

same as that recorded in these cases. The coloured impurities were removed by trituration with cold glacial acetic acid, then the insoluble material was collected, and finally purified by recrystallisation from dilute alcohol, to which a little hydrochloric acid had been added. *o*-Chlorophenol sulphoxide forms fine colourless needles, which melt at 165° , and are soluble in most hot organic media :

0.1594 gave 0.2600 CO_2 and 0.0383 H_2O . $\text{C} = 47.21$; $\text{H} = 2.83$.

0.1535 " 0.1415 AgCl . $\text{Cl} = 22.8$.

0.2032 " 0.1485 BaSO_4 . $\text{S} = 10.0$.

$\text{C}_{10}\text{H}_9\text{O}_3\text{Cl}_2\text{S}$ requires $\text{C} = 47.52$; $\text{H} = 2.73$; $\text{Cl} = 23.4$; $\text{S} = 10.5$ per cent.

The substance dissolves in concentrated sulphuric acid, forming a blue solution, from which the colour is removed by the addition of a phenolic ether, a sulphonium base being then formed. The action of alcoholic hydrogen chloride on this substance is somewhat different from that observed in the preceding cases. After the usual treatment, the reaction mixture was submitted to distillation in a current of steam. The white, crystalline solid which separated from the distillate was evidently dichlorophenol, for it melted at 43° and contained 43.4 per cent. of chlorine (calc., $\text{Cl} = 43.55$ per cent.). The non-volatile portion consisted of an oil which resisted all attempts at purification ; it apparently consisted of a mixture of polychloro-sulphides.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of these experiments.

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CCXXXVII.—Some Phenolic Derivatives of β -Phenylethylamine.

By GEORGE BARGER AND ARTHUR JAMES EWINS.

p-HYDROXY- β -PHENYLETHYLAMINE, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, which is formed by the action of micro-organisms from tyrosine and from proteins containing tyrosine, has been shown to have a pronounced physiological activity (Barger and Walpole, *J. Physiol.*, 1909, 38, 343) ; it is, for instance, one of the active constituents of ergot extracts (Barger, *Trans.*, 1909, 95, 1123).

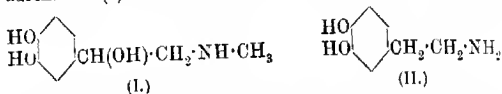
Since the effect of this base on the vascular system and on certain organs is essentially similar to that of adrenaline (Dale and Dixon, *J.*

Physiol., 1909, **39**, 25), to which *p*-hydroxy- β -phenylethylamine is also chemically related, an examination of a considerable number of similarly constituted amines was undertaken by Dale in order to trace as far as possible the connexion between physiological activity and chemical structure within the limits of this group (Barger and Dale, *J. Physiol.*, 1910, **41**, 19).

The present paper deals with the synthesis of some of these amines. They were chosen for the following reasons:

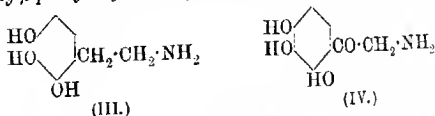
(1) Since the bactericidal action of phenol is greatly enhanced by the introduction of a methyl group into the benzene ring (yielding cresol), we prepared 3-methyl-4-hydroxy- β -phenylethylamine. The pressor action of this base was found, however, to be only about one half as great as that of the parent substance.

(2) One of the differences between *p*-hydroxy- β -phenylethylamine and adrenaline (I) is that the former substance has only a single



phenolic hydroxyl group as compared with two in the latter substance. We therefore prepared 3:4-dihydroxy- β -phenylethylamine (II), which was found to be scarcely more active than the monophenolic amine although its *N*-methyl derivative, obtained by Pyman from an oxidation product of laudanosine (this vol., p. 268), approximates much more closely to adrenaline.

(3) Since in several cases the introduction of a second phenolic hydroxyl group greatly increases the physiological activity of bases of this type, we wished to trace the effect of introducing yet another phenolic hydroxyl group, and for this purpose prepared 2:3:4-trihydroxy- β -phenylethylamine (III) and ω -aminogallacetophenone (IV)



Both these bases were somewhat less active than the corresponding dihydroxy-bases (namely, 3:4-dihydroxy- β -phenylethylamine and ω -aminoacetylcatechol).

The close chemical relationship of the bases (I), (II), (III), and (IV) is further illustrated by the fact that they all give the colour reaction hitherto described as characteristic for adrenaline (I) (Ewins, *J. Physiol.* 1910, **40**, 317).

The synthesis of 4-hydroxy- β -*m*-tolylethylamine started with *m*-tolyl acetonitrile, and was completely analogous to that of *p*-hydroxy-

phenylethylamine from phenylacetonitrile (Barger, Trans., 1909, 95, 1123).

3:4-Dihydroxy- β -phenylethylamine was obtained from its dimethyl ether, and has already been described by Mannich (Ber., 1910, 43, 196).

The production of the pyrogallol bases (III and IV) at first gave considerable difficulty. The 2:3:4-trihydroxybenzaldehyde required for (III) had to be prepared with anhydrous hydrogen cyanide according to Gattermann's method. It was found impossible to obtain 2:3:4-trimethoxy- β -phenylethylamine from 2:3:4-trimethoxyphenylpropionamide by Hofmann's reaction, although this method was employed in preparing the corresponding dimethoxy-base. We therefore had to use Curtius's method, starting from 2:3:4-trimethoxyphenylpropionylhydrazide.

In the case of ω -aminogallacetophenone (IV) we found it quite impossible to isolate a pure substance when ω -chlorogallacetophenone was acted on by ammonia, although this method is employed technically in the case of ω -chloroacetyl catechol; the substance is destroyed too readily in alkaline solution. We therefore had recourse to an indirect method; ω -chlorogallacetophenone reacts readily with sodium azide, and from the ω -triazogallacetophenone, $C_6H_4(OH)_3 \cdot CO \cdot CH_2 \cdot N_3$, thus produced the required amine is obtainable by reduction.

In the course of our work on this subject we have also prepared β -phenylethylmethylamine, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_3$, of which adrenaline is the trihydroxy-derivative. Two methods for preparing this base will be mentioned, although it is not a phenolic amine, and was recently prepared by Johnson and Guest (Amer. Chem. J., 1909, 42, 340) according to a third method (methylation of benzenesulphonylphenylethylamine and subsequent hydrolysis).

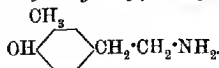
EXPERIMENTAL.

β -Phenylethylmethylamine, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_3$.

As the direct methylation of β -phenylethylamine yields a quaternary iodide, we condensed methylamine (in 33 per cent. aqueous solution) with phenylacetaldehyde by means of sodium hydroxide, and reduced the crude condensation product, which separated out, with sodium and alcohol. The base was isolated as the oxalate.

A second, and more convenient, method consists in acting on ethoxy- β -phenylethane, $C_6H_5 \cdot CH_2 \cdot CH_2Cl$ (Barger, Trans., 1909, 95, 2194), with an excess of a 33 per cent. alcoholic solution of methylamine at 100° for several hours. The base thus obtained was distilled (b. p. 265°), and its hydrochloride was analysed. (Found, Cl = 20.7. Calc., Cl = 20.4 per cent.)

Preparation of 4-Hydroxy-β-m-tolylethylamine,



p-Nitro-*m*-tolylacetonitrile, $\text{NO}_2 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{---} \end{array} \text{CH}_2 \cdot \text{CN}$.—Ten grams of *m*-tolylacetonitrile (Señkowski, *Monatsh.*, 1888, 9, 854) were dropped into 40 c.c. of nitric acid (D 1.5) at a temperature below -5° . The acid solution was then poured into water and extracted with ether. After washing with sodium carbonate, drying, and distilling, a fraction boiling at $201\text{--}205^\circ/22$ mm. was collected, which solidified, and on crystallisation from ether and light petroleum melted at 52° . The yield was 80 per cent. of the theoretical:

0.1584 gave 0.3554 CO_2 and 0.0665 H_2O . C = 61.2; H = 4.6.

$\text{C}_9\text{H}_9\text{O}_2\text{N}_2$ requires C = 61.4; H = 4.5 per cent.

p-Amino-*m*-tolylacetonitrile, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CN}$.—*p*-Nitro-*m*-tolylacetonitrile (19 grams) was dissolved in alcohol (240 c.c.), tin-foil (25 grams), and then gradually concentrated hydrochloric acid (120 c.c.) was added. The temperature was at first kept below 60° , finally being raised to 100° . After extraction with ether, the base was distilled, and 8.5 grams (60 per cent.) boiling at $175\text{--}183^\circ/20$ mm. were obtained. On crystallisation from benzene, the substance melted at 87° :

0.1552 gave 0.4204 CO_2 and 0.0902 H_2O . C = 73.9; H = 6.5.

$\text{C}_9\text{H}_{10}\text{N}_2$ requires C = 74.0; H = 6.8 per cent.

The *hydrochloride*, prepared by adding alcoholic hydrogen chloride to the ethereal solution of the base, melts at $247\text{--}248^\circ$:

0.2082 gave 0.1620 AgCl. Cl = 19.3.

$\text{C}_9\text{H}_{10}\text{N}_2 \cdot \text{HCl}$ requires Cl = 19.4 per cent.

The *oxalate* melts at $164\text{--}165^\circ$:

0.1884 gave 24 c.c. N_2 (moist) at 20° and 768 mm. N = 14.7.

$(\text{C}_9\text{H}_{10}\text{N}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ requires N = 14.7 per cent.

p-Hydroxy-*m*-tolylacetonitrile, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CN}$.—3.9 Grams of sodium nitrite dissolved in a little water were slowly added to a boiling solution of 8.5 grams of the amino-compound dissolved in 200 c.c. of dilute sulphuric acid (210 c.c. of water and 17 c.c. of concentrated sulphuric acid). On extracting the acid solution with ether, 2.5 grams (30 per cent.) of a substance were obtained, which distilled at $162\text{--}164^\circ/2$ mm. and crystallised in the receiver. It crystallises from benzene in leaflets melting at 84° :

0.1526 gave 0.4093 CO_2 and 0.0807 H_2O . $\text{C} = 73.1$; $\text{H} = 5.9$.
 0.1718 " 14.2 c.c. N_2 (moist) at 22° and 760 mm. $\text{N} = 9.4$.
 $\text{C}_9\text{H}_9\text{ON}$ requires $\text{C} = 73.5$; $\text{H} = 6.1$; $\text{N} = 9.5$ per cent.

CH_3
 4-Hydroxy- β -m-tolylethylamine, $\text{OH} \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_3 \end{array} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$.—0.9 Gram

of *p*-hydroxy-*m*-tolylacetonitrile yielded, on reduction with 4 grams of sodium in boiling alcoholic solution, 0.62 gram of a crude hydrochloride, which was crystallised by adding ether to its concentrated solution in alcohol. From this the free base was obtained; it crystallised from xylene, and, after sublimation in a vacuum, melted at 132 – 133° :

0.1290 gave 0.3364 CO_2 and 0.0910 H_2O . $\text{C} = 71.2$; $\text{H} = 7.9$.
 $\text{C}_9\text{H}_{13}\text{ON}$ requires $\text{C} = 71.5$; $\text{H} = 8.6$ per cent.

The hydrochloride was also analysed:

0.1226 gave 0.0956 AgCl . $\text{Cl} = 19.3$.

$\text{C}_9\text{H}_{13}\text{ON} \cdot \text{HCl}$ requires $\text{Cl} = 19.0$ per cent.

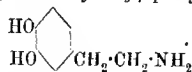
The dibenzoyl derivative crystallised from dilute alcohol in long, thin needles, melting at 130 – 131° .

The quaternary iodide, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2\text{I}$, was obtained by boiling the base with a little methyl alcohol and a large excess of methyl iodide. It melts at 231 – 232° , and closely resembles hordenine methiodide in solubility and other properties.

4-Hydroxy- β -*m*-tolylethylamine resembles *p*-hydroxy- β -phenylethylamine in behaviour and derivatives.

The physiological action of the former base is about one-half of the latter. Both bases give Millon's reaction, but it is significant that, unlike *p*-hydroxy- β -phenylethylamine, the tolyl compound does not give Mörner's reaction (green coloration after heating with sulphuric acid and formaldehyde). It would appear that substitution in the phenolic ring prevents this reaction from taking place.

Preparation of 3:4-Dihydroxy- β -phenylethylamine,



3:4-Dimethoxy- β -phenylethylamine was prepared from vanillin according to the method described in detail by Pictet and Finkelstein (*Ber.*, 1909, 42, 1979), and 5.2 grams of the amine boiling at 164 – $166^\circ/13$ mm. were obtained from 20.5 grams of homoveratric acid.

The amine was hydrolysed by heating with ten parts of concentrated hydrochloric acid to 170° for two hours. The hydrochloride so obtained crystallised from 90 per cent. alcohol in glistening, almost colourless

plates, melting and decomposing at 240—241°. Yield, 45 per cent. of the theoretical. (Found, C=50.6; H=6.2. Calc., C=50.7; H=6.2 per cent.

The *hydrobromide* was obtained by heating the dimethoxy-amine to 130° for two hours with ten times its weight of concentrated aqueous hydrobromic acid. The crystalline hydrobromide was obtained quite pure in the same manner as that employed in the preparation of the hydrochloride. The salt crystallises in plates, melting at 212°;

0.1212 gave 0.0984 AgBr. Br=34.5.

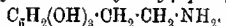
$C_8H_{12}O_2NBr$ requires Br=34.2 per cent.

The aqueous solution of the salts of 3:4-dihydroxy- β -phenylethylamine gave an intense green coloration with ferric chloride.

The quaternary chloride, $C_8H_8(OH)_2 \cdot CH_2 \cdot CH_2 \cdot NMe_3Cl$, was prepared in order to compare its action with that of hordenine methiodide, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3I$. The action of the two substances is very similar, like that of nicotine, and unlike that of adrenaline.

3:4-Dihydroxy- β -phenylethyltrimethylammonium chloride was obtained from 3:4-dimethoxy- β -phenylethylamine. The quaternary iodide obtained by treating the latter base with methyl iodide was transformed into the chloride by digestion with silver chloride, and was then hydrolysed by concentrated hydrochloric acid at 170°. On removal of the latter, the residue crystallised from alcohol and ether, and melted at 201°.

Preparation of 2:3:4-Trihydroxy- β -phenylethylamine,



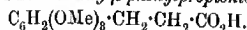
2:3:4-Trimethoxybenzaldehyde, $C_6H_3(OMe)_3 \cdot CHO$.—This aldehyde does not appear to have been described before, although F. Mauthner (*Ber.*, 1909, 42, 188) has stated that it can be obtained from 2:3:4-trimethoxyphenylglyoxylic acid by the action of aniline. The methylation of 2:3:4-trihydroxybenzaldehyde, which was prepared from pyrogallol and anhydrous hydrocyanic acid according to Gattermann and Kœbner's method (*Ber.*, 1899, 32, 281), was carried out in an atmosphere of hydrogen by the method employed by Perkin and Robinson (*Trans.*, 1907, 91, 1079) for the preparation of veratraldehyde from vanillin. Twenty-five grams of 2:3:4-trihydroxybenzaldehyde were dissolved in 80 c.c. of methyl alcohol, and to this solution was added 24 grams of sodium hydroxide dissolved in the minimum quantity of water. The solution became very dark brown in colour. Eighty grams of methyl sulphate were then added, and when the vigorous reaction had nearly subsided, a further 66 grams in small quantities alternately with small quantities of sodium hydroxide were added at such a rate that a vigorous reaction was maintained.

The mixture was kept for half an hour, and then poured into 500 c.c. of water. An oil separated, which was extracted by means of ether, and, after drying and removal of the solvent, the residue was distilled. 18.5 Grams of a colourless liquid, boiling at $168-170^{\circ}/12$ mm., were thus obtained. The distillate solidified after some time to a crystalline mass of long, thin needles, melting at 30° .

0.1840 gave 0.4126 CO_2 and 0.1020 H_2O . $\text{C} = 61.1$; $\text{H} = 6.2$.

$\text{C}_{10}\text{H}_{12}\text{O}_4$ requires $\text{C} = 61.2$; $\text{H} = 6.1$ per cent.

2:3:4-Trimethoxy- β -phenylpropionic Acid,

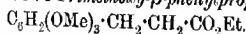


Twenty grams of 2:3:4-trimethoxybenzaldehyde were dissolved in 35 grams of ethyl acetate, and the solution added to 3.3 grams of finely divided sodium contained in a large flask provided with a reflux condenser. A vigorous reaction ensued. The product was kept for one hour, and then a solution of 14 grams of sodium hydroxide in methyl alcohol was added. After the reaction had ceased, 250 c.c. of water were added. The alcohol was then removed by evaporation on a water-bath, water being added from time to time to avoid undue concentration. The alkaline solution was then reduced by the addition of 500 grams of $2\frac{1}{2}$ per cent. sodium amalgam in small portions, concentrated hydrochloric acid being added from time to time to neutralise the excess of sodium hydroxide formed in the reaction. The resulting solution was filtered, and acidified with hydrochloric acid. A yellow oil separated, which slowly crystallised. The acid was purified by distillation under diminished pressure (it boils at $200-203^{\circ}/2$ mm.) and subsequent crystallisation from ether and light petroleum, from which it separated in clusters of prisms, melting at 76° . Yield, 50 per cent. of the theoretical:

0.2150 gave 0.4722 CO_2 and 0.1282 H_2O . $\text{C} = 59.9$; $\text{H} = 6.6$.

$\text{C}_{12}\text{H}_{16}\text{O}_5$ requires $\text{C} = 60.0$; $\text{H} = 6.7$ per cent.

Ethyl 2:3:4-Trimethoxy- β -phenylpropionate,



The acid obtained as above was converted into the corresponding ethyl ester by dissolving in five times its weight of 5 per cent. alcoholic hydrogen chloride and boiling under reflux for six hours. The alcohol and hydrochloric acid were evaporated off, and the residue was distilled. The ester boils at $200-201^{\circ}/20$ mm. Yield, 70 per cent. of the theoretical:

0.2671 gave 0.4797 CO_2 and 0.1390 H_2O . $\text{C} = 63.1$; $\text{H} = 7.4$.

$\text{C}_{14}\text{H}_{18}\text{O}_5$ requires $\text{C} = 62.7$; $\text{H} = 7.4$ per cent.

2 : 3 : 4-Trimethoxy- β -phenylpropionylhydrazide Hydrochloride,
 $C_6H_3(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2 \cdot HCl$.

Two grams of the above ester were gradually added to 0.6 gram of boiling hydrazine hydrate. Solution was complete at the end of one hour, and the solution was boiled under reflux for several hours longer. The excess of hydrazine was removed by evaporation in a vacuum over sulphuric acid. The syrupy residue could not be crystallised, but on dissolving in alcohol and adding a little alcoholic hydrogen chloride a crystalline precipitate separated, which was increased by the addition of ether. The hydrochloride thus obtained was recrystallised from 98 per cent. alcohol, separating in the form of hexagonal plates, which melted at 155° :

0.1679 gave 0.3020 CO_2 and 0.0947 H_2O . $C = 49.0$; $H = 6.3$.

$C_{12}H_{10}O_4N_2Cl$ requires $C = 48.8$; $H = 6.5$ per cent.

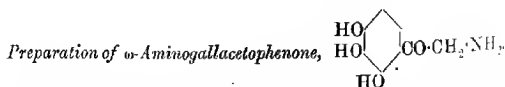
The solution of this salt readily reduced ammoniacal silver in the cold, and Fehling's solution on boiling.

2 : 3 : 4-Trihydroxy- β -phenylethylamines Hydrochloride,
 $C_6H_2(OH)_3 \cdot CH_2 \cdot CH_2 \cdot NH_2 \cdot HCl$.

The hydrazide obtained as described above was diazotised at 0° . The crude azide, obtained by extraction with ether, was converted into the corresponding urethane derivative by boiling in absolute alcoholic solution for twelve hours under reflux. The alcohol was then distilled off, and the residue hydrolysed by heating in a sealed tube with concentrated hydrochloric acid to 170 – 180° for three hours. The very dark-coloured contents of the tube were evaporated to dryness, dissolved in a little water, boiled with animal charcoal, filtered, and the solution evaporated nearly to dryness. From the dark brown syrupy product, crystals slowly separated. These were pressed on a plate, and recrystallised from absolute alcohol by addition of ether. The crystals, which melted at 162 – 163° , were still dark brown in colour. The aqueous solution gives with ferric chloride a deep purple brown coloration, which rapidly fades:

0.1000 gave 0.0700 $AgCl$. $Cl = 17.32$.

$C_8H_{11}O_3NCl$ requires $Cl = 17.35$ per cent.



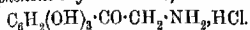
ω -Triazogallacetophenone, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot N_3$.—Seven grams of ω -chlorogallacetophenone, prepared according to Nencki's method

(*J. Russ. Phys. Chem. Soc.*, 1883, 25, 182), were dissolved in 50 c.c. of hot water, and a hot solution of 2.5 grams of sodium azide in a little water added. On cooling, a crystalline solid separated. This was collected and recrystallised from xylene, when thumb-shaped plates, melting at 155°, were obtained. Yield, 50 per cent. of the theoretical:

0.2460 gave 44.2 c.c. N_2 (moist) at 19° and 758 mm. $N = 20.7$.

$C_5H_7O_4N_3$ requires $N = 20.1$ per cent.

ω-Aminogallacetophenone Hydrochloride,



—Five grams of *ω*-triazogallacetophenone were dissolved in absolute alcohol. Ten grams of tin-foil were then placed in the liquid, and 60 c.c. of concentrated hydrochloric acid added in small portions. As reduction proceeded, the hydrochloride of the base separated out in small, rectangular plates. The yield was 1.2 grams, or 25 per cent. of the theoretical.

For analysis, the salt was recrystallised from alcohol and ether, when it melted at 259–260°:

0.1916 gave 10.8 c.c. N_2 (moist) at 17° and 754 mm.

0.1275 „ 0.0838 AgCl. $Cl = 16.2$; $N = 6.5$.

$(C_8H_{10}O)_2NCl$ requires $N = 6.4$; $Cl = 16.1$ per cent.

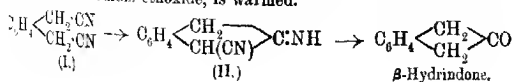
The salt is readily soluble in water; its aqueous solution darkens on keeping, and with very dilute ferric chloride solution gives a dirty green coloration, which rapidly changes to a brownish-yellow.

THE WELLSOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HEINE HILL, S.E.

CCXXXVIII.—The Formation and Reactions of Imino-compounds. Part XIV. The Formation of *α*-Hydrindone and its Derivatives.

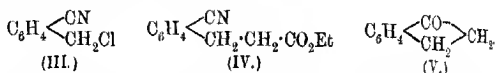
By ALEC DUNCAN MITCHELL AND JOCELYN FIELD THORPE.

ONE time ago (TRANS., 1908, 93, 165) it was shown that *β*-hydrindone and some of its derivatives could be derived from *β*-imino-*α*-cyano-*γ*-hydrindene (II), a substance which is formed in quantitative yield when an alcoholic solution of *o*-phenylenediacetonitrile (I), containing a trace of sodium ethoxide, is warmed.



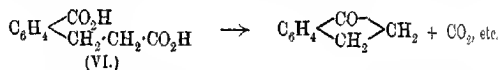
The present paper deals with a similar reaction by which α -hydrindone and its derivatives can be produced through the imino-compound.

α -Hydrindone was originally prepared by Gabriel and Hausmann (*Ber.*, 1889, 22, 2018), and was subsequently investigated by Hausmann (*ibid.*, p. 2020). Gabriel and Hausmann prepared the ketone by condensing *o*-cyanobenzyl chloride (III) with the sodium compound of ethyl acetoacetate, when a compound, which they considered to be ethyl *o*-cyano- β -phenylpropionate (IV), was formed, and this substance, on treatment with concentrated hydrochloric acid, passed into α -hydrindone (V).



Hausmann (*loc. cit.*) subsequently found that when ethyl sodio-malonate was used in this reaction in place of ethyl sodioacetoacetate, the same substance (IV) was produced.

The formation of α -hydrindone from ethyl *o*-cyano- β -phenylpropionate on treatment with concentrated hydrochloric acid was explained on the assumption that *o*-carboxy- β -phenylpropionic acid (VI) is first formed, which then decomposes into water, carbon dioxide, and α -hydrindone, thus:



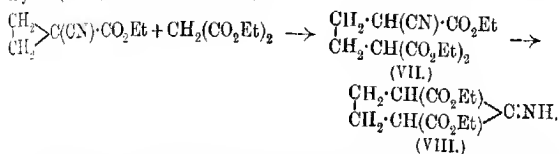
This is also the explanation advanced by Aschan (*Chemie der Alicyclischen Verbindungen*, p. 1028), who remarks that König has shown (*Annalen*, 1893, 275, 341) that *o*-carboxy- β -phenylpropionic acid passes on distillation into α -hydrindone. It must be remembered, however, that the production of α -hydrindone from *o*-carboxy- β -phenylpropionic acid in this manner takes place at a high temperature, that is to say, under conditions very different from those which convert ethyl *o*-cyano- β -phenylpropionate into this ketone. It therefore seemed to us unlikely that the mechanism of this reaction, as recorded above, could be correct, and we consequently decided to seek for some other explanation more in accordance with the experimental facts.

It has been already mentioned that, according to the observation of Hausmann, the condensation of *o*-cyanobenzyl chloride with both ethyl sodio-malonate and ethyl sodioacetoacetate yields the same product, namely, ethyl *o*-cyano- β -phenylpropionate (IV). It is evident, therefore, that in the first condensation a carbethoxyl group, and in the second condensation an acetyl group, must have been eliminated during the process of the condensation.

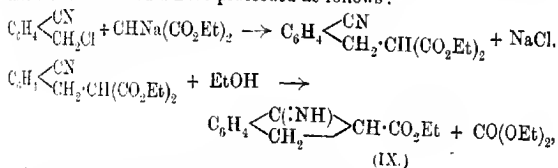
Neither Gabriel nor Hausmann seems to have remarked on this, but

in the light of recent investigation on the formation of five-ring imino-compounds, the fact possessed for us some significance.

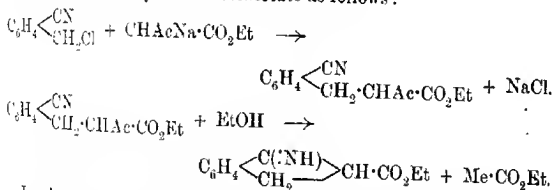
Thus we have always found that when the five-carbon ring is formed through the imino-group, the formula of the product does not allow of two carboxyl groups, a nitrile group and a carboxyl group, or an acetyl group and a carboxyl group, being attached to the same carbon atom; an example of this, which bears closely on the present instance, being the transformation of the open-chain compound (VII), which is formed by the condensation of ethyl sodiomalonate and ethyl 1-cyano-cyclopropane-1-carboxylate into ethyl 2-iminocyclopentane-1:3-dicarboxylate (VIII) (this vol., p. 1002).



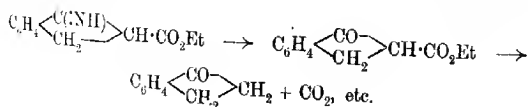
The elimination of a carboxyl group in Hausmann's condensation suggested therefore the closing of the five-carbon ring, in which case the reaction would have proceeded as follows:



or in the case of ethyl sodioacetoacetate as follows:

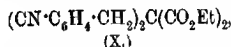


In these circumstances the compound described by Gabriel and Hausmann as ethyl *o*-cyano- β -phenylpropionate would be ethyl 1-imino-hydrindene-2-carboxylate (IX), and its transformation into α -hydrindone by the action of concentrated hydrochloric acid could be readily explained thus:



Investigation proved that this view of the formation of α -hydrindone was correct, and that the compound described as ethyl *o*-cyano- β -phenylpropionate behaved in every way as an imino-compound of formula (IX). Before this fact could be definitely proved it was necessary, however, to thoroughly study the condensation of *o*-cyanobenzyl chloride with the sodium compounds of both ethyl malonate and ethyl acetoacetate, and as, at the same time, it was thought advisable, for reasons given later, to investigate the corresponding condensation with ethyl sodiumcyanoacetate, it is best, for the sake of comparison, to describe the three condensations separately.

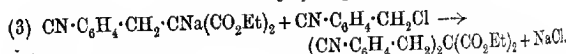
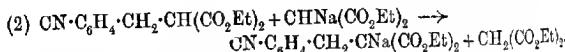
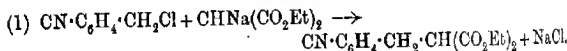
(1) *The Condensation of o-Cyanobenzyl Chloride with the Sodium Compound of Ethyl Malonate.*—In effecting this condensation, Hausmann used equivalent quantities of sodium dissolved in alcohol, and of the two reacting substances. He found that, mixed with the chief product of the condensation (the so-called ethyl *o*-cyano- β -phenylpropionate), a considerable quantity of a product melting at 86° was also formed. This he showed to be ethyl di-*o*-cyanobenzylmalonate (X),



which had been formed by the condensation of two molecules of *o*-cyanobenzyl chloride with one molecule of ethyl malonate.

Hausmann separated the two products by treating the mixture with cold concentrated hydrochloric acid, in which the supposed ethyl *o*-cyano- β -phenylpropionate dissolved, and could be obtained on mixing the hydrochloric acid filtrate with water.

Now it is obvious that the formation of the derivative (X) must have taken place in the following manner :



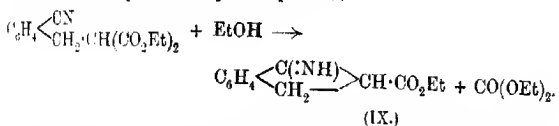
That is to say, the initial condensation product of *o*-cyanobenzyl chloride and ethyl sodiummalonate must be the normal product of the formula $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, and the elimination of a carboxyl group must therefore have taken place subsequent to its formation.

Our previous experiments on this point show that the elimination of this group is always effected by the action of free sodium ethoxide, or of some sodium derivative dissociating in alcoholic solution, and hence it seemed to us likely that by preventing, so far as possible, the presence

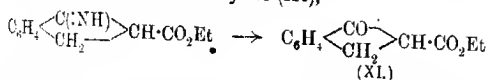
of excess of the sodium derivative of ethyl malonate during the process of the condensation the elimination of this group might be avoided.

This proved to be the case, for it was found that when an alcoholic solution of ethyl sodiomalonate containing a slight excess of ethyl malonate was added slowly to a hot alcoholic solution of *o*-cyanobenzyl chloride, the product of the reaction did not become solid on being poured into water, but remained as a heavy oil at the bottom of the liquid.

This oil proved to be the normal condensation product, namely, ethyl *o*-cyanobenzylmalonate, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, and it was found that when an alcoholic solution of this substance containing a trace of sodium ethoxide was warmed, a carbethoxyl group was at once eliminated as ethyl carbonate, and the product described by Hausmann as ethyl *o*-cyano- β -phenylpropionate was formed. Subsequent investigation proved conclusively that this product is ethyl 1-iminohydrindene-2-carboxylate (IX), and that its formation in the manner described above is represented by the equation:



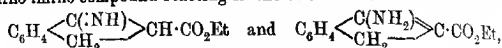
The proof of the constitution of this substance is as follows: When a solution of the imino-compound in alcohol is mixed with rather more than the quantity of concentrated hydrochloric acid necessary to hydrolyse the C:NH-group to carbonyl and the solution is warmed, ammonium chloride separates, and the solution on dilution yields an oil which boils at 185°/20 mm., and which gives in alcoholic solution an intense violet coloration with ferric chloride. This oil, which is without doubt ethyl 1-hydrindone-2-carboxylate (XI),



gives a well defined phenylhydrazone and semicarbazone, the same phenylhydrazone being also formed from the imino-compound (IX) when it is boiled in acetic acid solution with phenylhydrazine acetate.

The imino-compound is, as Gabriel and Hausmann showed, readily soluble in concentrated hydrochloric acid, and is precipitated on adding water. It is not, however, completely unchanged by this process, since a quantity, depending for amount on the length of time it is left in contact with the strong acid, is converted into the ketone. The process of conversion at the ordinary temperature is very slow, and the usual method adopted in other cases, of pouring the concentrated hydro-

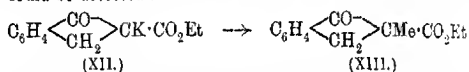
chloric solution into hot water and cooling, converts only a small quantity of the imino-compound into the ketone. It is evident therefore that ethyl 1-iminohydrindene-2-carboxylate is a tautomeric amino-imino-compound reacting in the two forms:



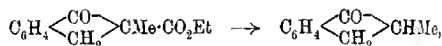
but that it has only a short imino-phase.

Ethyl 1-hydrindone-2-carboxylate (XI) is readily soluble in dilute aqueous potassium hydroxide, but it is only slowly extracted from its solution in ether by means of aqueous sodium carbonate solution. Both the potassium and sodium salts are sparingly soluble in excess of the alkali, and can be readily isolated in a pure condition.

When the potassium salt (XII), either in the soluble or insoluble form, is boiled in alcohol with methyl iodide, the *C*-methyl derivative (XIII) is obtained as sole product, and no trace of the corresponding *O*-methyl ether could be detected:

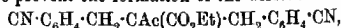


The *C*-methyl derivative readily yields the corresponding 2-methyl-1-hydrindone when distilled in a current of steam from dilute sulphuric acid,



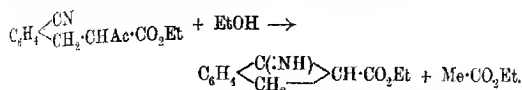
a process which is complete, owing to there being no tendency for the β -alkyl derivatives of α -hydrindone to undergo intramolecular condensation analogous to the formation of anhydro-bis- α -hydrindone (Trans., 1897, 71, 241) from α -hydrindone. The direct formation of ethyl 1-iminohydrindene-2-carboxylate in the original condensation is, we find, best effected by working in the manner described above until the reaction is complete, and then, by adding excess of sodium ethoxide, to convert the open-chain compound into the hydrindene ring. The compound $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CN}$, which is formed by the condensation of two molecules of *o*-cyanobenzyl chloride with one molecule of ethyl malonate, is so readily produced that if the condensation is effected in the usual way, the product consists for the most part of the more complex derivative.

(2) *The Condensation of Ethyl Sodioacetoacetate and o-Cyanobenzyl Chloride.*—It is hardly necessary in this condensation to take any precautions to prevent the formation of the derivative



as under the ordinary conditions very little of it is formed. If, however, the method described in the experimental portion is used, the normal product (XII) can be readily isolated, and this compound on

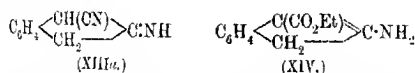
(treatment with a trace of sodium ethoxide passes quantitatively into ethyl acetate and ethyl 1-iminohydrindene-2-carboxylate, thus :



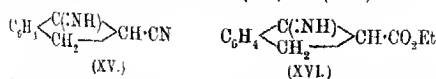
For the rapid preparation of this imino-compound in quantity this condensation produces the best results, the best method being to add an alcoholic solution of ethyl sodioacetoacetate containing a slight excess of sodium ethoxide to a hot alcoholic solution of the chloride.

(3) *The Condensation of Ethyl Sodicyanoacetate and o-Cyanobenzyl Chloride.*—The main object of investigating this condensation was to compare the derivatives of α -hydrindone with those of β -hydrindone in order to ascertain whether the phenomenon of "steric inhibition" which was so marked in the case of the β -compound substituted in the α -position applied also to the α -compound substituted in the β -position.

It has been found as regards the derivatives of β -hydrindone and its imino-derivative (Trans., 1908, 93, 165), that the presence of certain groups on the α -carbon atom causes the compounds to react as true amino-derivatives, whereas certain other groups on this carbon atom cause the imino-form to be stable, and that this occurs irrespective of the additivity of the groups which we have hitherto shown to be the determining factor in deciding the amino- or imino-structure of a compound of this type. Thus the compound of formula (XIIIa) evidently had the imino-structure, or rather exhibited amino-imino-tautomerism with a long imino-phase, whereas when the cyano-group was displaced by the less negative carbethoxyl group, the compound, instead of showing amino-imino-tautomerism with a longer imino-phase, as it should have done, behaved as a true amino-compound of formula (XIV) :



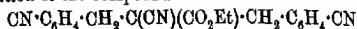
It seemed of interest therefore to compare the corresponding derivatives of α -iminohydrindene of formulae (XV) and (XVI)



in order that a direct comparison might be made between the two series.

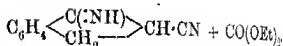
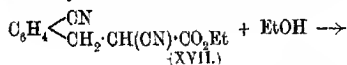
The condensation of *o*-cyanobenzyl chloride with the sodium

compound of ethyl cyanoacetate, if carried out in the usual way, leads to the formation of the compound



to the extent of 80 per cent. of the theoretical amount, and only a small quantity of ethyl 1-imino-2-cyanohydrindene (XV) is produced.

If, however, the precaution is taken of adding an alcoholic solution of the sodium salt of ethyl cyanoacetate to a hot alcoholic solution of *o*-cyanobenzyl chloride, a considerable yield of the normal condensation product (XVII) can be obtained, and this substance on treatment with sodium-ethoxide passes at once into 1-imino-2-cyanohydrindene and ethyl carbonate in accordance with the scheme:

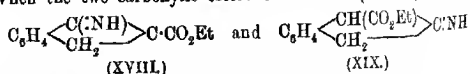


A comparison of 2-imino-1-cyanohydrindene (XIII) with 1-imino-2-cyanohydrindene (XV) showed that these compounds did not possess any essential points of difference beyond what was to be expected from their structure. Thus the imino-group of 1-imino-2-cyanohydrindene is between the negative phenylene group and the nitrile group, whereas in the case of 2-imino-1-cyanohydrindene the negative influence of the phenylene group would be less pronounced. Consequently it might be anticipated that whilst both compounds would be tautomeric amino-imino-compounds, the 1-imino-derivative would possess a longer amino-phase than the 2-imino-derivative.

This anticipation is borne out by the experimental facts, for whereas 1-imino-2-cyanohydrindene, with its long amino-phase, dissolves readily in concentrated hydrochloric acid, forming a salt which, on the addition of water, is dissociated regenerating the amino-compound mixed with only a small quantity of the corresponding ketone, 2-imino-1-cyanohydrindene does not dissolve in concentrated hydrochloric acid, but when warmed with the acid is converted almost completely into the ketone. In other words, the rate of hydrolysis of the 2-imino-derivative is very much quicker than that of the 1-imino-derivative.

The two compounds therefore serve as admirable examples of the influence of negative groups on the predominance of the amino- or imino-phase in compounds exhibiting amino-imino-tautomerism.

When the two carboxylic esters of formulae (XVIII) and (XIX)



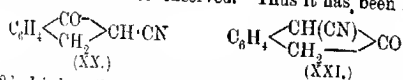
are compared, a marked difference is at once apparent.

It has been already shown that ethyl 2-iminohydrindene-1-car

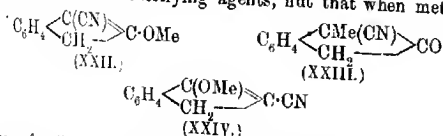
oxylate (XIX) is a true amino-compound, which can be hydrolysed to the corresponding acid by means of hydrochloric acid without the nitrogen group being affected. Subsequent experiments showed that this behaviour was exhibited by other compounds having groups of large molecular volume attached to the 1-carbon atom, and hence it was suggested that the presence of a group of more than a certain volume did not permit of the attachment of the hydrogen atom to the 1-carbon atom. In other words, the compound ceased, under these conditions, to react in one of its tautomeric forms.

The examination of the behaviour of ethyl 1-iminohydrindene-2-carboxylate (XVIII) under similar conditions showed that, although the substitution of the carbethoxyl group for the nitrile group increased the amino-phase of the compound, that is to say, increased the length of time required for the hydrolysis of the compound to the ketone, yet it still exhibited well-defined amino-imino-tautomerism, and its hydrolysis to the ketone by acids was always completely effected. It is, of course, evident that as the carbethoxy-group possesses less negative properties than the nitrile group, the reverse should be the case, and it therefore follows that there must be a certain degree of steric hindrance attaching to the 1-carbon atom, but to a very much less extent than to the 2-carbon atom. An explanation of this fact is afforded by the consideration that the 1-carbon atom of ethyl 2-iminohydrindene-1-carboxylate is attached to both the phenylene group and the carbethoxyl group, whereas the 2-carbon atom of ethyl 1-iminohydrindene-2-carboxylate has only the carbethoxyl attached to it.

When the oxygen derivatives (XX) and (XXI) are compared, certain points of difference are also observed. Thus it has been shown that

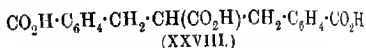
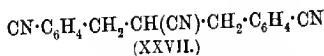
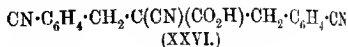
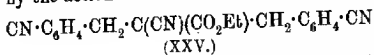


1-cyano-2-hydrindone (XXI) yields a methoxy-derivative (XXII) when alkylated by the usual etherifying agents, but that when methylated

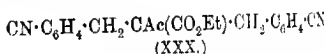
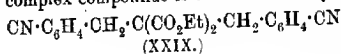


by means of sodium methoxide and methyl iodide it yields the C-methyl derivative (XXIII). With 2-cyano-1-hydrindone (XX) the increased negative character of the compound due to the proximity of the phenylene group is apparent, and the action of sodium methoxide and methyl iodide leads to the formation of the methoxy-derivative (XXIV) only.

As considerable quantities of the compounds containing two equivalents of *o*-cyanobenzyl chloride had accumulated during the preparation of the simpler products formed in these condensations, we investigated their properties. The cyano-derivative (XXV) formed in the ethyl cyanoacetate condensation is readily hydrolysed by dilute alkali, yielding an alkali salt, from which the acid (XXVI) is obtained by the action of mineral acids. When heated at 180°, this substance



eliminates carbon dioxide and passes into the trinitrile (XXVII). When completely hydrolysed, the nitrile is converted into the tri-carboxylic acid (XXVIII), a compound which is identical with that formed by the complete hydrolysis of the condensation products (XXIX) and (XXX) formed in the ethyl malonate and ethyl acetoacetate condensations respectively. The constitution of these more complex compounds is therefore clearly established.



EXPERIMENTAL.

Ethyl o-Cyanobenzylmalonate, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$

This substance can be prepared in quantity by the condensation of ethyl sodiomalonate with *o*-cyanobenzyl chloride if care is taken not to have free sodium ethoxide present at any time during the course of the condensation. In order to effect this, it is necessary to add an alcoholic solution of the sodium compound of ethyl malonate to a hot alcoholic solution of the chloride, that is to say, in the reverse manner to that usually adopted in these condensations. The conditions found most favourable were as follows: 2.2 grams of sodium were dissolved in 50 c.c. of alcohol and mixed with 16 grams of ethyl malonate, the warm solution being then slowly added to a hot solution of 15 grams of *o*-cyanobenzyl chloride dissolved in the requisite amount of alcohol. The reaction was allowed to proceed by its own heat, and was completed by heating on the water-bath for five minutes, when the solution was found to be neutral. Water was then added, and the alcohol and unchanged ethyl malonate separated by distillation

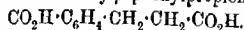
in a current of steam, the heavy, non-volatile oil being subsequently extracted by ether. The residue which remained after evaporating the ether yielded a large fraction, boiling at $213^{\circ}/20$ mm., consisting of a viscid, colourless oil :

0.1958 gave 0.4722 CO_2 and 0.1080 H_2O . $\text{C} = 65.77$; $\text{H} = 6.13$.

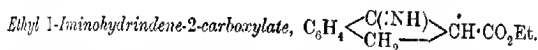
$\text{C}_{15}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C} = 65.4$; $\text{H} = 6.2$ per cent.

The ethyl salt is unchanged by cold concentrated hydrochloric acid, and its open-chain structure is proved by the fact that when boiled for a long time with dilute sulphuric acid, it is slowly hydrolysed, and the solution on cooling deposits a crystalline acid, which, when recrystallised from water, yields long needles, melting at 166° . (Found, $\text{C} = 61.72$; $\text{H} = 5.3$. Calc., $\text{C} = 61.8$; $\text{H} = 5.2$ per cent.)

The acid is therefore *o*-carboxy- β -phenylpropionic acid,



During the fractionation of ethyl *o*-cyanobenzylmalonate a small quantity of lower boiling material was obtained, which solidified after some time, and, on examination, proved to be ethyl 1-iminohydrindene-2-carboxylate (see p. 2273). There was also a small amount of higher fraction boiling at about $300^{\circ}/20$ mm., which also solidified, and proved on investigation to be ethyl di-*o*-cyanobenzylmalonate (see p. 2280).



This substance may be prepared in one of two ways, namely :

(1) *By the Action of Alcoholic Sodium Ethoxide on Ethyl o-Cyanobenzylmalonate.*—This method, which gives a quantitative yield of the imino-compound, can be carried out as follows : 10 grams of the ethyl salt are diluted with twice its volume of alcohol, and 1 c.c. of a solution of 1 gram of sodium in 12 c.c. of alcohol is added. The solution, which becomes appreciably warm, is kept for fifteen minutes, when it is warmed on the water-bath for five minutes and then poured into an equal volume of water. The crystals which separate are then collected and recrystallised from dilute alcohol.

The mother liquor from the crystals was extracted with ether, and the residue, after evaporating the ether, carefully fractionated under the ordinary pressure. A fraction boiling at $126\text{--}127^{\circ}$ was ultimately obtained, which analysis showed to be ethyl carbonate. (Found, $\text{C} = 50.65$; $\text{H} = 8.6$. Calc., $\text{C} = 50.8$; $\text{H} = 8.5$ per cent.)

(2) *By the Direct Condensation of Ethyl Sodiomalonate and o-Cyanobenzyl Chloride.*—This method was that used by Gabriel and Hausmann, but under the conditions employed by them, we find that the greater portion of the product consists of ethyl di-*o*-cyanobenzylmalonate, and only a small yield of the imino-compound can be obtained. It is men-

tioned later (p. 2279) that the heat method for preparing this imino-compound in quantity is by employing the sodium compound of ethyl acetoacetate instead of ethyl sodiomalonate in the condensation, because in that case very little of the di-derivative is formed. A good yield of the imino-compound can, however, be obtained from ethyl malonate if the conditions described in the preparation of ethyl *o*-cyanobenzylmalonate (p. 2270) are closely followed, and, as soon as the condensation mixture has become neutral, a small quantity of alcoholic sodium ethoxide is added, and the heating continued for five minutes longer. When the product obtained in this way is poured into water, it will be found that the whole of the dicarboxylic ester has been converted into the imino-compound and ethyl carbonate, and that it will deposit a large quantity of oil which will solidify on scratching. This solid, which consists of the imino-compound mixed with some ethyl di-*o*-cyanobenzylmalonate, can be separated by the method used by Gabriel and Hausmann, that is, by dissolving the imino-compound in concentrated hydrochloric acid and filtering the solution from the undissolved di-derivative. On diluting the filtrate, a certain amount of the imino-compound separates in the crystalline form, but the separation is by no means complete, as the substance is appreciably soluble in dilute hydrochloric acid. In order to obtain the whole amount, it is necessary to extract the diluted acid solution with ether.

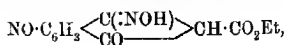
Ethyl 1-iminohydrindene-2-carboxylate crystallises from dilute alcohol in colourless needles, which melt at 98°. It gives no coloration with ferric chloride:

0.1923 gave 0.4970 CO₂ and 0.1060 H₂O. C = 70.49; H = 6.10.

C₁₂H₁₃O₂N requires, C = 70.9; H = 6.4 per cent.

The mother liquor from the recrystallisation of the imino-compound gives an intense blue coloration with ferric chloride, showing that the treatment with hydrochloric acid had converted some of it into the corresponding ketone. When treated in hot acetic acid solution with phenylhydrazine acetate it yields the same hydrazone, melting at 101.5°, as that derived from the ketone (p. 2273). It is insoluble in aqueous potassium hydroxide, and is only slowly hydrolysed on boiling with this reagent.

Action of Nitrous Acid.—When the imino-compound is dissolved in concentrated hydrochloric acid and mixed when very cold with excess of sodium nitrite solution, an oil is precipitated which solidifies after some time. When this substance is recrystallised from alcohol, it is obtained in brilliant yellow leaflets, which melt at 163° with vigorous decomposition and charring. Analysis points to the formula



but the position of the nitroso-group in the ring is uncertain :

0.1765 gave 0.3559 CO_2 and 0.0632 H_2O . $\text{C} = 54.99$; $\text{H} = 3.95$.

$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C} = 55.0$; $\text{H} = 3.8$ per cent.

Ethyl 1-hydrindone-2-carboxylate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$.

Ethyl 1-iminohydrindone-2-carboxylate is only very slightly changed when its solution in concentrated hydrochloric acid is poured into boiling water, conditions which completely hydrolyse the corresponding nitrile to the ketone (see p. 2277). The hydrolysis can, however, be completely effected in the following manner: Ten grams of the imino-compound are dissolved in 50 c.c. of alcohol, and rather more than the calculated quantity of concentrated hydrochloric acid is added. The solution is then boiled for three minutes, during which time a large quantity of ammonium chloride separates. It is then cooled and mixed with a large volume of water, when a heavy oil is deposited, which is extracted by ether. The ethereal solution, when freed from impurities by washing first with water and then with sodium carbonate solution, leaves, on evaporation, an oil which distils at $185^\circ/20$ mm. as a rigid, colourless liquid. The distillation can only be accomplished with small quantities, otherwise rapid decomposition ensues :

0.2169 gave 0.5593 CO_2 and 0.1168 H_2O . $\text{C} = 70.33$; $\text{H} = 5.98$.

$\text{C}_{12}\text{H}_{12}\text{O}_3$ requires $\text{C} = 70.6$; $\text{H} = 5.9$ per cent.

Ethyl 1-hydrindone-2-carboxylate gives in alcoholic solution an intense blue coloration with ferric chloride. It is soluble in dilute aqueous potassium hydroxide and in cold alkaline carbonate solutions, but it cannot be extracted from its solution in ether by shaking with these reagents. When excess of aqueous potassium hydroxide is added to a solution of the ketone in the dilute alkali, a sparingly soluble potassium salt separates. When freshly precipitated, this salt is readily soluble in both ethyl and methyl alcohol, but if the solution in either of these solvents is kept, colourless, silky needles separate, which are very sparingly soluble in hot alcohol :

0.3192 gave 0.1127 K_2SO_4 . $\text{K} = 15.83$.

$\text{C}_{12}\text{H}_{11}\text{O}_3\text{K}$ requires $\text{K} = 16.1$ per cent.

It is probable that the salt when first precipitated contains water of crystallisation, although no satisfactory analysis could be made of the hydrated product.

The *phenylhydrazone*, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$, is formed when either the ketone or the imino-compound, dissolved in glacial acetic acid, is mixed with a solution of phenylhydrazine acetate and boiled. It separates as an oil on dilution, and solidifies on scratching. When recrystallised from alcohol, it forms pale yellow needles, which melt at 101.5° :

0.1861 gave 0.5001 CO_2 and 0.1036 H_2O . $\text{C} = 73.30$; $\text{H} = 6.13$.

$\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 73.5$; $\text{H} = 6.1$ per cent.

The semicarbazone, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_3$, is precipitated when a solution of the ketone in dilute alcohol is mixed with an aqueous solution of semicarbazide acetate. It crystallises from dilute acetic acid in slender needles, which melt and char at 200° :

0.1445 gave 0.3161 CO_2 and 0.0756 H_2O . $\text{C} = 59.66$; $\text{H} = 5.81$.

$\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_3$ requires $\text{C} = 59.8$; $\text{H} = 5.8$ per cent.

1-Hydrindone-2-carbanilide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{NHPh}$, is formed when the ethyl salt is boiled with an equal volume of aniline for five minutes and the solution is poured into dilute hydrochloric acid. It crystallises from alcohol in colourless, lustrous plates, which melt at 177° :

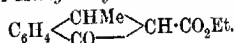
0.1560 gave 0.4369 CO_2 and 0.0754 H_2O . $\text{C} = 76.38$; $\text{H} = 5.37$.

$\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C} = 76.5$; $\text{H} = 5.2$ per cent.

a-Hydrindone.

This ketone is most conveniently prepared by passing a current of steam through ethyl 1-hydrindone-2-carboxylate or the imino-compound suspended in boiling 10 per cent. sulphuric acid. The ketone passes over with the steam, and solidifies in the receiver. It melted at 41° , and was characterised by conversion into the semicarbazone melting at 237° . The formation of anhydro-bishydrindene was not observed, the yield of the ketone being practically quantitative.

Ethyl 3-Methyl-1-hydrindone-2-carboxylate,



This compound may be prepared in the following way: Eight grams of ethyl 1-hydrindone-2-carboxylate are added to a solution containing 1 gram of sodium dissolved in 20 c.c. of alcohol, when a copious precipitation of the sodium salt takes place. Excess of methyl iodide is then added, and the mixture is heated on the water-bath until the sodium compound, which is practically insoluble in hot alcohol, has all passed into solution. The product is then freed from alcohol by evaporation on the water-bath, diluted with water, and the oil which is then precipitated is extracted by ether. The ethereal extract, after being washed with sodium carbonate solution, is dried and evaporated, when it leaves an oil which distils at $181^\circ/20$ mm. as a moderately viscid, colourless liquid:

0.1848 gave 0.4817 CO_2 and 0.1848 H_2O . $\text{C} = 71.09$; $\text{H} = 6.70$.

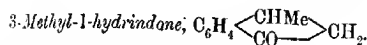
$\text{C}_{18}\text{H}_{18}\text{O}_3$ requires $\text{C} = 71.6$; $\text{H} = 6.4$ per cent.

Ethyl 3-methyl-1-hydrindone-2-carboxylate is insoluble in aqueous potassium hydroxide, and gives no coloration in alcoholic solution with ferric chloride.

The *semicarbazone*, $C_{14}H_{17}O_3N_3$, is precipitated when a solution of the ketone in dilute alcohol is mixed with an aqueous solution of semicarbazide acetate. It separates from dilute methyl alcohol in clusters of small needles, which melt at 150° :

0.1632 gave 0.3794 CO_2 and 0.0956 H_2O . $C = 61.14$; $H = 6.28$.

$C_{14}H_{17}O_3N_3$ requires $C = 61.1$; $H = 6.2$ per cent.



This substance is formed when ethyl 3-methyl-1-hydrindone-2-carboxylate, suspended in 20 per cent. sulphuric acid, is treated with a current of steam. The ketone, as it is formed, passes over with the steam, and can be obtained as a colourless liquid, boiling at $250^\circ/756$ mm., on extracting the distillate with ether:

0.1693 gave 0.5118 CO_2 and 0.1080 H_2O . $C = 82.46$; $H = 7.01$.

$C_{10}H_{16}O$ requires $C = 82.2$; $H = 6.8$ per cent.

The *phenylhydrazone*, $C_{18}H_{16}N_2$, separates as an oil, which solidifies on scratching, when a hot solution of the ketone in dilute acetic acid is mixed with a hot solution of phenylhydrazine acetate. It crystallises from dilute alcohol in glistening yellow plates, melting at 35° :

0.1684 gave 0.5025 CO_2 and 0.1035 H_2O . $C = 81.27$; $H = 6.69$.

$C_{16}H_{16}N_2$ requires $C = 81.4$; $H = 6.8$ per cent.

The *semicarbazone*, $C_{11}H_{13}ON_3$, prepared in the usual way, crystallises from dilute alcohol in slender needles, melting at 190° :

0.1049 gave 0.2493 CO_2 and 0.0614 H_2O . $C = 64.81$; $H = 6.50$.

$C_{11}H_{13}ON_3$ requires $C = 65.0$; $H = 6.4$ per cent.

Ethyl α -o-Dicyano- β -phenylpropionate, $CN \cdot C_6H_4 \cdot CH_2 \cdot CH(CN) \cdot CO_2Et$.

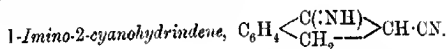
—The condensation of *o*-cyanobenzyl chloride with the sodium compound of ethyl cyanoacetate, if carried out in the usual manner, yields very little of the above product or of ethyl 1-imino-2-cyano-hydrindene, the chief compound formed being ethyl α -*oo*-tricyano- $\beta\beta$ -diphenylisobutyrate, which is produced to the extent of about 80 per cent. of the theoretical quantity. If, however, the condensation is effected in the following manner, a good yield of the normal product can be obtained: Two grams of sodium are dissolved in 50 c.c. of alcohol, and 10.3 grams of ethyl cyanoacetate are added, the solution being kept warm in order to prevent the sodium compound from

caking. The hot sodium compound is then added to a hot solution of 13.5 grams of *o*-cyanobenzyl chloride in 20 c.c. of alcohol, and the mixture kept hot until the reaction is finished. The bulk of the alcohol is then distilled off, and the residue diluted with water, when an oil separates which becomes partly solid. On extracting with ether, the solid, which was found to be ethyl α -*o*-tricyano- $\beta\beta$ -diphenylisobutyrate (see p. 2280), remains undissolved, and can be separated from the ethereal solution of the oil by filtration. The residue left on evaporating the dried ethereal extract is then distilled under diminished pressure. It is a viscid, colourless liquid, which boils at $220^{\circ}/20$ mm.:

0.1921 gave 0.4844 CO_2 and 0.0934 H_2O . $\text{C} = 68.77$; $\text{H} = 5.40$.

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 68.9$; $\text{H} = 5.3$ per cent.

*Ethyl α -*o*-dicyano- β -phenylpropionate* does not dissolve in cold concentrated hydrochloric acid. Its structure is shown by the formation of *o*-carboxy- β -phenylpropionic acid from it on complete hydrolysis with dilute sulphuric acid.



This substance may be prepared either by the action of sodium ethoxide on ethyl α -*o*-dicyano-*p*-phenylpropionate, or by the direct condensation of *o*-cyanobenzyl chloride with the sodium compound of ethyl cyanoacetate in the presence of excess of sodium ethoxide.

(1) *From Ethyl α -*o*-Dicyano- β -phenylpropionate*.—In this preparation 10 grams of the dicarboxylic ester are dissolved in 25 c.c. of alcohol, and mixed with 1 c.c. of a solution of sodium ethoxide containing 1 gram of sodium dissolved in 10 c.c. of alcohol. The solution, which becomes brown in colour, is then warmed on the water-bath for five minutes, when it is cooled and diluted with an equal volume of water. Crystals separate on scratching, which, when recrystallised from benzene, form large prisms, melting at 137° .

The mother liquor from the condensation, when extracted by ether, yields a residue on evaporating the solvent, which when carefully fractionated furnishes a considerable amount of ethyl carbonate, boiling at 126° . (Found, $\text{C} = 50.58$; $\text{H} = 8.61$. Calc., $\text{C} = 50.8$; $\text{H} = 8.5$ per cent.)

(2) *From Ethyl Sodicyanoacetate and *o*-Cyanobenzyl Chloride*.—This method of preparation always yields the imino-nitrile mixed with some ethyl α -*o*-tricyano- $\beta\beta$ -diphenylisobutyrate, from which it cannot be readily separated. If the ketone is required, it can be quickly isolated pure by this means, because it is only necessary to treat the mixture with hot dilute hydrochloric acid, extract with ether, and shake out the ketone by means of sodium carbonate solution, in order

to obtain the pure product on acidifying the alkaline extract. Owing to the ease with which the imino-compound is hydrolysed to the ketone by hydrochloric acid, it is not advisable to separate the mixture by the aid of this reagent. Ultimately the following process was found to give satisfactory results.

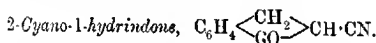
The condensation was effected in the same manner as described for ethyl α -o dicyano-*p*-phenylpropionate (see p. 2275), and when the reaction was finished a slight excess of sodium ethoxide was added and the heating continued for fifteen minutes. Water was then added, and the solid which separated was collected. It was then rubbed with cold methyl alcohol, filtered from the undissolved di-derivative, and precipitated from the methyl-alcoholic solution by the addition of water.

After this process had been repeated twice, the dried product was recrystallised from benzene, when it was obtained in large prisms, melting at 137° :

0.1898 gave C 53.46 CO_2 and 0.0907 H_2O . C = 76.83; H = 5.31.

$\text{C}_{10}\text{H}_8\text{N}_2$ requires C = 76.9; H = 5.1 per cent.

1-Imino-2-cyanohydrindene is at once soluble in cold concentrated hydrochloric acid. When treated in hot acetic acid solution with a solution of phenylhydrazine acetate, it yields the same hydrazone as 2-cyano-1-hydrindone (see p. 2278).



This compound is readily prepared from 1-imino-2-cyanohydrindene by hydrolysis with dilute hydrochloric acid, for which purpose the following conditions were found to give the best results. Ten grams of the imino-compound were dissolved in concentrated hydrochloric acid, and the clear solution poured into twice its volume of boiling water, the solution being cooled as quickly as possible after the addition of the acid. An oil separated, which was extracted by ether, the ethereal extract being shaken with dilute sodium carbonate solution. The alkaline extract was then acidified, when an oil was precipitated which solidified on scratching. When collected and recrystallised from dilute alcohol, it formed small, colourless needles, melting at 73° :

0.1738 gave 0.4845 CO_2 and 0.0712 H_2O . C = 76.03; H = 4.55.

$\text{C}_{10}\text{H}_7\text{ON}$ requires C = 76.4; H = 4.5 per cent.

2-Cyano-1-hydrindone is readily soluble in dilute alkaline carbonate solutions. When dissolved in dilute aqueous potassium hydroxide, the potassium salt separates on the addition of excess of the alkali. The ketone gives a green coloration in alcoholic solution with ferric chloride.

The *phenylhydrazone*, $C_{16}H_{13}N_3$, is precipitated when a solution of the ketone in dilute acetic acid is warmed with a solution of phenylhydrazine acetate. It separates from alcohol in pale yellow needles, melting at 160° :

0.1797 gave 0.5110 CO_2 and 0.0851 H_2O . $C = 77.55$; $H = 5.26$.

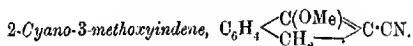
$C_{16}H_{13}N_3$ requires $C = 77.7$; $H = 5.3$ per cent.

The *O-benzoyl* derivative, $C_{17}H_{11}O_2N$, can be prepared in small yield by the Schotten-Baumann method. It crystallises from alcohol in long, colourless needles, melting at 101.5° :

0.1355 gave 0.3884 CO_2 and 0.500 H_2O . $C = 78.16$; $H = 4.10$.

$C_{17}H_{11}O_2N$ requires $C = 78.1$; $H = 4.2$ per cent.

When 2-cyano-1-hydrindone is boiled with dilute sulphuric acid (10 per cent.) for five hours and the product is distilled in a current of steam, α -hydrindone is formed, and passes over with the steam.



The above methoxy-derivative is the sole product of the methylation of 2-cyano-1-hydrindone whether the alkylation is carried out by means of sodium methoxide and methyl iodide or whether the pure potassium salt is used for the purpose. The preparation can be conveniently effected as follows: The potassium salt prepared by the addition of excess of potassium hydroxide to a solution of the ketone in dilute alkali is purified by rubbing with cold ethyl alcohol, and is then suspended in methyl alcohol and treated with excess of methyl iodide. The mixture is heated on the water-bath until all the salt has passed into solution, when it is evaporated on the water-bath and treated with water. The oil which is then precipitated is extracted with ether, and the ethereal extract dried and evaporated. The residue distils at $185^\circ/20$ mm. as a clear, colourless oil, which is quite insoluble in cold alkali:

0.2013 gave 0.5691 CO_2 and 0.0978 H_2O . $C = 77.11$; $H = 5.4$.

$C_{11}H_9ON$ requires $C = 77.2$; $H = 5.3$ per cent.

The methoxy-structure of the compound is clearly shown by its behaviour on hydrolysis, for when it is treated with warm aqueous potassium hydroxide it slowly dissolves, and when the solution is acidified a crystalline substance melting at 73° is deposited. This compound was shown by direct comparison to be identical with 2-cyano-1-hydrindone.



The conditions employed in preparing this substance were as follows: 21.7 Grams of ethyl acetoacetate were added to an alcoholic

solution containing 3.5 grams of sodium, and the mixture slowly added while hot to a hot solution of 25 grams of *o*-cyanobenzyl chloride in 25 c.c. of alcohol. The reaction was vigorous, and when all the sodium compound had been added, the product was found to give a neutral reaction. The greater portion of the alcohol was then distilled off and the residue mixed with water, when an oil separated, which was extracted by ether. The product obtained, after evaporating the dried ethereal solution, boiled at 210°/20 mm., forming a viscid, colourless liquid:

0.1972 gave 0.4947 CO₂ and 0.1100 H₂O. C = 68.47; H = 6.19.
 C₁₄H₁₃O₂N requires C = 68.6; H = 6.1 per cent.

Ethyl o-cyano-α-benzylacetoacetate is not affected by cold concentrated hydrochloric acid, and on complete hydrolysis with dilute sulphuric acid yields *o*-carboxy-β-phenylpropionic acid.

The Transformation of Ethyl o-Cyano-α-benzylacetoacetate into Ethyl 1-Iminohydrindene-2-carboxylate.

This conversion was effected by the action of sodium ethoxide in the following manner: Ten grams of the ester were dissolved in alcohol, treated with 1 c.c. of a 10 per cent. solution of sodium ethoxide in alcohol, and then warmed on the water-bath for fifteen minutes. At the end of this time the solution, which had a strong odour of ethyl acetate, was mixed with water, and the solid which then separated was filtered. When recrystallised from dilute alcohol it was melted at 98°, and was proved, by direct comparison, to be identical with ethyl 1-iminohydrindene-2-carboxylate.

The aqueous mother liquor from the condensation was saturated with ammonium sulphate and extracted with ether, the ethereal extract being washed with calcium chloride solution to remove alcohol, dried, and fractionated. The fraction boiling at 78° was collected, and proved from its odour and analysis to be ethyl acetate. (Found, C = 54.49; H = 9.21. Calc., C = 54.7; H = 9.1 per cent.)

When ethyl 1-iminohydrindene-2-carboxylate is required in large quantities, the best method for its preparation is the direct condensation of ethyl sodioacetoacetate and *o*-cyanobenzyl chloride in the presence of a slight excess of sodium ethoxide, because in this condensation the formation of the di-derivative does not take place to any appreciable extent. The product of the condensation, which solidifies on pouring into water, is separated in a pure condition by dissolving in concentrated hydrochloric acid, filtering, and extracting the filtrate after dilution with water with ether. The yield of ethyl 1-iminohydrindene-2-carboxylate under these conditions is 80 per cent. of the theoretical.

*The Di-o-cyanobenzyl Derivatives Formed in the Foregoing
Condensations.*

Ethyl di-o-cyanobenzylmalonate, $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{C}(\text{CO}_2\text{Et})_2$, and ethyl di-o-cyanobenzylacetoacetate, $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{C}(\text{Ac} \cdot \text{CO}_2\text{Et})_2$, obtained as by-products in the condensations of o-cyanobenzyl chloride with ethyl sodiomalonate and ethyl sodioacetoacetate respectively, have been prepared and described by Gabriel and Hausmann (*loc. cit.*), but they were not further investigated. The following is a description of the products which these compounds yield on hydrolysis, as well as of those derived from ethyl α -oo-tricyano- $\beta\beta$ -diphenylisobutyrate, which has not been prepared before.

Ethyl α -oo-Tricyano- $\beta\beta$ -diphenylisobutyrate,
 $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

This substance is obtained as a by-product in the condensation of ethyl sodiocyanacetate with o-cyanobenzyl chloride, and remains undissolved after the imino-nitrile has been separated by the method described on page 2276. It separates from alcohol in small, colourless needles, melting at 123° :

0.2121 gave 0.5695 CO_2 and 0.1002 H_2O . $\text{C} = 73.27$; $\text{H} = 5.25$.

$\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}_3$ requires $\text{C} = 73.5$; $\text{H} = 5.0$ per cent.

The ester is sparingly soluble in ether.

α -oo-Tricyano- $\beta\beta$ -diphenylisobutyric Acid,
 $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{C}(\text{CN}) \cdot \text{CO}_2\text{H}.$

When ethyl α -oo-tricyano- $\beta\beta$ -diphenylisobutyrate is warmed with aqueous potassium hydroxide, it passes into solution, and if, when all has dissolved, the solution is cooled, an oily potassium salt separates, which dissolves on the addition of more water. On acidification, the clear solution deposits an oil which solidifies on stirring, and the solid can then be recrystallised from hot alcohol, from which solvent it separates as a microcrystalline powder melting at 175° with vigorous evolution of gas:

0.1508 gave 0.3988 CO_2 and 0.0569 H_2O . $\text{C} = 72.12$; $\text{H} = 4.18$.

$\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3$ requires $\text{C} = 72.4$; $\text{H} = 4.1$ per cent.

oo-Dicyano- $\beta\beta$ -diphenylisobutyronitrile, $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CN}.$

This substance is formed when the above carboxylic acid is heated at 170° in a bath of sulphuric acid until all carbon dioxide has been evolved. The dark-coloured residue solidifies on being rubbed with

ether, and at the same time becomes colourless. It may be further purified by recrystallisation from methyl alcohol, from which solvent it separates in large, flattened needles, melting at 132–133°:

0.1733 gave 23.2 c.c. N_2 at 18° and 733 mm. $N = 15.3$.

$C_{18}H_{18}N_2$ requires $N = 15.5$ per cent.

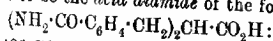
The trinitrile is readily soluble in hot methyl or ethyl alcohol and in hot benzene. It is sparingly soluble in ether or light petroleum.

oo-Dicarboxy-ββ-diphenylisobutyric Acid,
 $(CO_2H \cdot C_6H_4 \cdot CH_2)_2CH \cdot CO_2H$.

This acid is formed by the ultimate hydrolysis of the di-o-cyanobenzyl derivatives described above.

From Ethyl α-oo-Tricyano-ββ-diphenylisobutyrate.—The ester is dissolved in concentrated sulphuric acid, and water is added until the solution just remains clear, when it is boiled on the sand-bath until an oil begins to separate. More water is then added until the solution is clear, when it is again heated until oil begins to separate. This process is continued for two hours, when the solution, which on cooling deposits large quantities of oil, is extracted by ether. When the ethereal extract is shaken with aqueous sodium carbonate and the alkaline extract acidified, a gummy acid is precipitated, which readily solidifies when rubbed with methyl alcohol, and crystallises from dilute alcohol in small needles, melting at 210°.

From Ethyl Di-o-cyanobenzylmalonate.—When this ester is boiled with an alcoholic solution containing one and a-half times the quantity of potassium hydroxide calculated for complete hydrolysis, and the heating is continued until all ammonia has apparently been given off, the solution on evaporating and acidifying yields a resinous acid. When this resin is extracted by ether, a large quantity of crystalline solid remains undissolved by the ether, and can be isolated by filtration. It can be recrystallised from much hot water, and is then obtained in small needles, melting at 227°. The analysis and properties of this substance showed it to be the *acid diamide* of the formula



0.1820 gave 0.4430 CO_2 and 0.0942 H_2O . $C = 66.33$; $H = 5.76$.

$C_{18}H_{18}O_4N_2$ requires $C = 66.3$; $H = 5.5$ per cent.

The following titration was also made: 0.2600 required 8.1 c.c. of $N/10$ -NaOH for neutralisation, whereas this amount of a monobasic acid, $C_{18}H_{18}O_4N_2$, requires 8.00 c.c.

The acid diamide when boiled for some time with excess of aqueous potassium hydroxide evolves ammonia, and the solution on acidifying yields a gummy acid, which solidifies on rubbing with alcohol. When recrystallised from dilute alcohol it forms small needles, melting at

210°, which are identical with those of the acid prepared from ethyl α -oo-tricyano- $\beta\beta'$ -diphenylisobutyrate:

0.1735 gave 0.4190 CO_2 and 0.0777 H_2O . $\text{C} = 65.86$; $\text{H} = 4.97$.

$\text{C}_{18}\text{H}_{16}\text{O}_6$ requires $\text{C} = 65.9$; $\text{H} = 4.9$ per cent.

The ethereal solution after the separation of the above acid diamide yields an oily residue on evaporation, which solidifies when rubbed with alcohol. It crystallises from dilute alcohol in yellow prisms, which melt at 142°, and yields a semicarbazone melting at 256°. We have not as yet succeeded in assigning any satisfactory formula to these substances.

Some of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

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CCXXXIX.—*Lead Silicates in Relation to Pottery Manufacture. Part II.*

By SIR EDWARD THORPE AND CHARLES SIMMONDS.

SOME years ago, in connexion with the question of lead poisoning in the pottery industry, we made a study of various complex lead silicates employed in the production of ceramic glazes ("Lead Silicates in Relation to Pottery Manufacture," Trans., 1901, 79, 792). In particular, we showed that the quantity of lead which could be dissolved from a silicate by dilute acids depended primarily on the type of silicate. Monosilicates are easily attackable. Polysilicates and disilicates are but slightly so, and this is the case whether they contain little or much lead. We further showed that in the case of the polysilicates and disilicates, as ordinarily prepared, there is frequently a small quantity of an easily soluble lead compound mixed with the bulk; this could be extracted with dilute acid, leaving the residue practically unattackable under the conditions of the experiment.

A fairly complete summary of present knowledge of lead silicates and glazes in respect of the foregoing properties has recently been published by Beck, Löwe, and Stegmüller,* who have studied the action

* "Zur Kenntniss der bleihaltigen Glasuren und deren Bleibgabe an saure Flüssigkeiten" (*Arbeit. K. Gesundheitsamts*, 1910, 33, No. 2).

of acids both on the powdered silicate and on the fused glaze as it exists on the finished pottery ware. With certain modifications, they have repeated our experiments; but whereas our studies, made on silicates in actual commercial use, were of necessity chiefly concerned with the complex silicates, containing not only lead but other bases, Beck, Löwe, and Stegmüller have adopted what in some respects is the better plan of studying first the simple lead silicates.

The results they obtain lead, however, to the same conclusions as our own. Thus the proportion of lead oxide dissolved from three simple silicates was found to be as follows:

| Silicate | PbO present grams | PbO dissolved by 1 per cent. HNO_3 | |
|-----------------------------------|----------------------|---|----------------------------|
| | | Amount | Percentage of total PbO |
| PbO, SiO_2 | 1.529 | 1.525 | 99.7 |
| $\text{PbO}, 2\text{SiO}_2$ | 1.232 | 0.106 | 8.6 |
| $\text{PbO}, 3\text{SiO}_2$ | 1.033 | 0.019 | 1.9 |

That is, practically all the lead is dissolved from the monosilicate, but a relatively small quantity only from the disilicate and trisilicate.

On a further treatment of the di- and tri-silicate residues, very little additional lead was extracted (0.5 and 0.6 per cent. respectively). This confirms what has already been stated (*loc. cit.*, p. 802).

An explanation of the fact that a single treatment with acid extracts substantially the whole of the "soluble" lead from the di- and the tri-silicates is suggested by the German authors. At the temperature of fusion a certain amount of dissociation may occur; thus the disilicate PbSi_2O_6 may partly dissociate into $\text{PbO} + 2\text{SiO}_2$, or into $\text{PbSiO}_3 + \text{SiO}_2$, and a portion of these components may remain dissociated when the silicate cools. Since both lead oxide and monosilicate are readily soluble in dilute acids, they would, if the silicate were sufficiently finely powdered, be all extracted on a single treatment with acid, whilst even from a relatively coarse powder the bulk of this "soluble" lead would be removed.

In the paper quoted we give a table (pp. 796—797) illustrating the fact that whether a lead silicate yields much soluble lead or not depends mainly on the value of the ratio: number of acidic molecules/number of basic molecules. Beck, Löwe, and Stegmüller remark that whilst this appears capable of rendering good service for rapid sorting-out purposes, it gives no special insight into the effect of a particular constituent in individual cases. They note that the effects of boric oxide and alumina are contrary to what would be expected from the table, and suggest that the possibility of the formation of complex borosilicates and aluminosilicates may have been overlooked. Also they remark that the possibility of alumina acting as an acidic oxide must not be excluded (*loc. cit.*, p. 226).

The authors in question, however, have quoted the table from a

Parliamentary Paper in which it was reproduced ("Lead Compounds in Pottery," 1901, Cd. 679, p. 26—27). On reference to the original paper already referred to (*loc. cit.*, p. 799), it will be seen that the points they mention had not been lost sight of. We note there that "subsidiary factors may exist in the possible different states of combination in which alumina and boric oxide may occur in the silicate"; and we also say "it is conceivable that in some cases the alumina may act as an acid constituent. In such cases, the amount of lead dissolved would presumably be less than indicated by the value of the ratio." Further on we briefly discussed the influence of boric oxide.

These views, put forward tentatively, were arrived at from a comparison of the results yielded by various complex silicates of very diverse composition; but it was recognised that the best way of studying the matter was to ascertain the effect of each oxide singly rather than to deduce it from such comparisons.

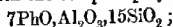
A number of silicates were therefore prepared by fusion of the ingredients in the proportions required for certain polysilicates and disilicates of definite formulae. These silicates, in a finely powdered condition, were then shaken continuously for an hour with 1000 times their weight of dilute hydrochloric acid (0.25 per cent.), and the quantity of lead dissolved was determined by a colorimetric method depending on the comparison of the depth of tint with that given by known quantities of freshly produced lead sulphide.

The results may be thus stated:

(I.) *Influence of Alumina.*

| | Polysilicates | | Disilicates | |
|--------------------------------------|---------------|-------|-------------|-------------|
| | (1) | (2) | (3) | (4) |
| SiO ₂ | 23.8 | 35.1 | 35.1 | 41.9 |
| PbO | 71.2 | 60.9 | 64.9 | 54.5 |
| Al ₂ O ₃ | — | 4.0 | — | 3.6 |
| | 100.0 | 100.0 | 100.0 | 100.0 |
| PbO dissolved | 25 | 5 | 5 | 5 per cent. |

No. 1 is the simple lead polysilicate $2\text{PbO}, 3\text{SiO}_2 (= 10\text{PbO}, 15\text{SiO}_2)$, and No. 2 corresponds with the complex polysilicate



thus the substitution in No. 2 of one molecule of Al_2O_3 for three molecules of PbO has had a very marked effect in decreasing the solubility of the lead.

No. 3 is the simple disilicate $\text{PbO}, 2\text{SiO}_2 (= 10\text{PbO}, 20\text{SiO}_2)$, and No. 4 is the complex disilicate $7\text{PbO}, \text{Al}_2\text{O}_3, 20\text{SiO}_2$. Here the substitution of Al_2O_3 for 3PbO has not affected the proportion of soluble lead, or at least, not sufficiently to be evident under the

conditions of the experiment. A similar conclusion appears to have been arrived at recently by H. Eisenlohr (*Sprechsaal*, 1910, 43, 389).

(II.) *Influence of Sodium Oxide.*

| | Polysilicate (5) | Disilicate (6) |
|-------------------------|---------------------|-------------------|
| SiO ₂ | 31.0 | 37.9 |
| PbO | 65.9 | 58.8 |
| Na ₂ O | 3.1 | 3.3 |
| | <hr/> 100.0 | <hr/> 100.0 |
| PbO dissolved | 44 | 13 per cent. |

No. 5 is the polysilicate $2\text{Na}_2\text{O}, 12\text{PbO}, 21\text{SiO}_2$; it is to be compared with No. 1 ($=14\text{PbO}, 21\text{SiO}_2$).

No. 6 is the disilicate $\text{Na}_2\text{O}, 5\text{PbO}, 12\text{SiO}_2$; its comparison sample is No. 3 ($=6\text{PbO}, 12\text{SiO}_2$); thus in both cases the substitution of one molecule of Na₂O for one of PbO has materially increased the proportion of soluble lead.

(III.) *Influence of Alumina and Sodium Oxide Together.*

| | Polysilicate (7) | Disilicate (8) |
|--------------------------------------|---------------------|-------------------|
| SiO ₂ | 33.8 | 40.4 |
| PbO | 62.3 | 56.2 |
| Al ₂ O ₃ | 2.4 | 2.1 |
| Na ₂ O | 1.5 | 1.3 |
| | <hr/> 100.0 | <hr/> 100.0 |
| PbO dissolved | 3½ | 5 per cent. |

No. 7 is the polysilicate $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 12\text{PbO}, 24\text{SiO}_2$. It is to be compared with No. 1 and No. 2, also with No. 5. Relatively to No. 1, a considerable lowering of the proportion of soluble lead has been effected, and this, in accordance with (I) and (II), is to be attributed to the alumina. As compared with No. 2, a larger quantity of soluble lead is shown, in agreement with the fact that No. 7 contains a smaller percentage of alumina than No. 2.

No. 8 is the disilicate $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 12\text{PbO}, 32\text{SiO}_2$. The proportion of soluble lead agrees with that in the simple disilicate No. 3.

(IV.) *Influence of Boron Trioxide.*

No borosilicates of definite molecular formulæ were made, but the following results were obtained with modifications of the simple disilicate:

| | Disilicate (1) | Modifications | |
|-------------------------------------|-------------------|---------------|--------------|
| | | (9) | (10) |
| SiO ₂ | 35.1 | 30 | 35 |
| PbO | 64.9 | 65 | 60 |
| B ₂ O ₃ | — | 5 | 5 |
| | 100.0 | 100 | 100 |
| PbO dissolved | 5 | 53 | 46 per cent. |

Thus the substitution of 5 per cent. of boron trioxide for the same quantity of either silica or lead oxide in the simple disilicate enormously increases the quantity of soluble lead. This effect, however, is not produced with the *complex* disilicates, or at least, not with those of a particular type. We had already noted (*loc. cit.*, p. 799) that from 4 to 6 per cent. of boron trioxide was present in certain borosilicates which yielded mere traces of lead to the action of solvents. But in these cases the proportion of silica was higher, and that of the lead oxide much lower, than in the two experiments above described, and notable quantities of lime and alumina were also present. Which of these factors determines the behaviour of the boron trioxide is at present obscure. It was precisely the influence of the various constituents that we had hoped to ascertain if the work had been completed.

The results obtained point clearly to the following conclusions:

(1) Alumina has a marked effect in promoting the stability of the polysilicates towards acids. Possibly this is due to its function in the silicate being that of an acidic oxide. In the disilicates this effect is less apparent, since these are already tolerably stable.

(2) Sodium oxide appears to increase the solubility of the lead, specially in the polysilicates.

(3) Boron trioxide in some cases renders the silicates much more easily attackable, but in others has no such effect.

Some experiments described by Beck, Löwe, and Stegmüller lead, in the main, to similar conclusions (*loc. cit.*, p. 214). With the simple lead silicates they mixed $2\frac{1}{2}$ or 5 per cent. of one or other of the following compounds: Al₂O₃, B₂O₃, CaO, Na₂B₄O₇. The mixtures were fused, and the proportion of soluble lead was determined in the resulting *complex* silicates. Since by this procedure the acidity of the original silicates is modified, the results are not closely comparable with those that we adduce. Thus the addition of 5 per cent. of lime to the disilicate raised the percentage of soluble lead from 5.3 to 20.0; but this experiment is not analogous to those we show in (II) with sodium oxide, because the new compound is notably more basic than the original, and would therefore in any case be expected to yield more soluble lead. Nevertheless, the general results obtained point in the

same direction as our own. Thus the effect of an addition of 5 per cent. of alumina could be traced in the decrease, by about 2 per cent., of the soluble lead in the disilicate (no experiments on the polysilicate are shown), and whilst 5 per cent. of borax raised the solubility figure of the disilicate from 5.3 to 32.0, the effect on the trisilicate was very slight, namely, an increase of only 1 per cent. Results of the same order were obtained with 5 per cent. of boron trioxide.

(CXL.—*The Colour and Absorption Spectra of Some Sulphur Compounds.*

By JOHN EDWARD PURVIS, HUMPHREY OWEN JONES, and
HUBERT SANDERSON TASKER.

In a previous paper (Jones and Tasker, *Trans.*, 1909, 95, 1904) the preparation and properties of some alkyl dithio-oxalates were described. These esters were found to exhibit a distinct yellow colour, whilst oxalates and oxalyl chloride are colourless.

The dithio-oxalates were found to have normal molecular weights in solution, so that it appears as if their colour had been produced owing to the replacement of oxygen by sulphur.

It was therefore decided to study the absorption spectra of these and some other sulphur compounds of similar structure in order to ascertain, if possible, the cause of the colour of thio-oxalates. The various ethyl and phenyl mono-, di- and tri-thiocarbonates were prepared and examined, as were also the corresponding dithio-oxalates, dithiomalonates, dithiosuccinates, and several other compounds containing two atoms of sulphur in the molecule. The results are described and discussed in this paper. We are not, at present, prepared to suggest a hypothesis to account for the results obtained; but those so far recorded for a number of coloured compounds of simple structure seem to be of value, and the publication of them may serve a useful purpose.

Each compound was obtained as pure as possible, its absorption spectrum studied in solution of various concentrations in pure ethyl alcohol, and the results are represented by curves in the usual way. A large number of the substances show no band due to selective absorption, and, in these cases, it will be sufficient if the reciprocals of the wave-lengths of the last transmitted lines at a thickness of 10 mm., and sometimes also of 2 mm., of solution be recorded; when the substance exhibits a band, the position of its head is also noted.

The following compounds were examined.

Thiocarbonates.

Diethyl thiocarbonate, $\text{OEt}\cdot\text{CO}\cdot\text{SEt}$, was prepared by the action of ethyl chlorocarbonate on sodium ethyl mercaptide (Salomon, *J. pr. Chem.*, 1873, [ii], 7, 255).

Diethyl thioncarbonate, $\text{OEt}\cdot\text{CS}\cdot\text{OEt}$, was prepared as described by Debus (*Annalen*, 1850, 75, 136), by the action of heat on ethyl xanthate, and was separated from the compound $\text{OEt}\cdot\text{CS}\cdot\text{SEt}$, which is formed at the same time, by repeated fractional distillation, until the product boiled between 161° and 161.5° .

Several analyses established the purity of the substance, which had a marked yellow colour. (For example: Found, $\text{S}=23.9$. $\text{C}_5\text{H}_{10}\text{O}_2\text{S}$ requires $\text{S}=23.9$ per cent.) We were not able to prepare this compound by the action of thiocarbonyl chloride on sodium or potassium ethoxide.

Diphenyl thioncarbonate, $\text{OPh}\cdot\text{CS}\cdot\text{OPh}$, was prepared by the action of thiocarbonyl chloride on aqueous sodium phenoxide (Bergreen, *Ber.*, 1888, 21, 346; Eckenroth and Koch, *Ber.*, 1894, 27, 1369).

The compound has been described as crystallising in colourless plates, but it was found that, after repeated recrystallisation from alcohol and other solvents, the compound still retained a very distinct cream colour. The colour was not intense, and small quantities of the substance might be taken to be colourless, whereas in large quantities the colour is unmistakable.

Diethyl dithiocarbonate, $\text{SEt}\cdot\text{CO}\cdot\text{SEt}$, was prepared by the action of carbonyl chloride on sodium ethylmercaptide (Salomon, *J. pr. Chem.*, 1872, [ii], 6, 443).

Diphenyl dithiocarbonate, prepared by the action of carbonyl chloride on sodium thiophenoxide, crystallises from alcohol in long needles, melting at 43° , and is quite colourless.

Diethyl thionthiocarbonate, $\text{OEt}\cdot\text{CS}\cdot\text{SEt}$, prepared by the action of ethyl bromide on potassium xanthate (Salomon, *loc. cit.*, p. 443), shows a distinct yellow colour very similar to that of diethyl thioncarbonate.

Diethyl trithiocarbonate, prepared by the action of thiocarbonyl chloride on sodium ethylmercaptide, is a deep reddish-orange liquid, boiling at $240^\circ/760$ mm. and at $118\text{--}119^\circ/10$ mm. (Debus, *Annalen*, 1850, 75, 147).

Diphenyl trithiocarbonate was prepared by the action of thiocarbonyl chloride on sodium thiophenoxide. It crystallises from alcohol in short prisms, melting at 43° , and showing a golden-yellow colour lighter than that of the ethyl compound:

0.1998 gave 0.4335 CO_2 and 0.0690 H_2O . $\text{C}=59.2$; $\text{H}=3.84$.

$\text{C}_{18}\text{H}_{10}\text{S}$ requires $\text{C}=59.5$; $\text{H}=3.82$ per cent.

Diethyl monothio-oxalate, prepared by the action of sodium ethylmercaptide on ethyl chloroglyoxylate ("chloroxalic ether"), as described by Morley and Saint (Trans., 1883, **43**, 400), is a liquid boiling at 216° , which shows a very pale yellow colour when examined in thick layers.

The various alkyl dithio-oxalates have already been described (Jones and Tasker, *loc. cit.*).

Diethyl dithiomalonate, prepared by the action of malonyl chloride on sodium ethylmercaptide, is a colourless liquid, boiling at $135^{\circ}/10$ mm. On distilling under atmospheric pressure, this ester appears to undergo decomposition with the formation of derivatives of ethyl mercaptan:

0.3421 gave 0.5443 CO_2 and 0.1894 H_2O . $\text{C}=43.4$; $\text{H}=6.15$.

$\text{C}_8\text{H}_{12}\text{O}_2\text{S}_2$ requires $\text{C}=43.8$; $\text{H}=6.25$ per cent.

Diphenyl dithiomalonate, prepared by the action of malonyl chloride on phenyl mercaptan or its lead salt, crystallises in long, colourless needles, melting at $94-94.5^{\circ}$:

0.2700 gave 0.6151 CO_2 and 0.1055 H_2O . $\text{C}=62.1$; $\text{H}=4.34$.

$\text{C}_{15}\text{H}_{12}\text{O}_2\text{S}_2$ requires $\text{C}=62.5$; $\text{H}=4.17$ per cent.

Diethyl dithiosuccinate, prepared by the action of succinyl chloride on sodium ethylmercaptide, is a colourless liquid, boiling at $165^{\circ}/10$ mm. The product when first formed was slightly fluorescent; the fluorescence persisted after distillation, but was removed by washing with dilute sodium hydroxide solution:

0.2355 gave 0.4010 CO_2 and 0.1465 H_2O . $\text{C}=46.4$; $\text{H}=6.91$.

$\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$ requires $\text{C}=46.6$; $\text{H}=6.8$ per cent.

Diphenyl dithiosuccinate, prepared by the action of succinyl chloride on phenyl mercaptan, crystallises from alcohol in colourless needles, melting at $90-90.5^{\circ}$:

0.1887 gave 0.4375 CO_2 and 0.0807 H_2O . $\text{C}=63.3$; $\text{H}=4.75$.

$\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}_2$ requires $\text{C}=63.6$; $\text{H}=4.64$ per cent.

It may be mentioned that succinyl chloride, which is described as a liquid, when pure sets to a crystalline solid, melting at 17° .

Ethyl ethylthioacetate, $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared from ethyl chloroacetate and sodium ethylmercaptide in the cold, is a colourless oil, boiling at $187-188^{\circ}$ (Claesson, *Bull. Soc. chim.*, 1875, [ii], **23**, 145).

Ethyl ethylthiothioacetate, $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{SEt}$, was prepared by the action of chloroacetyl chloride on sodium ethylmercaptide; the reaction was started in a freezing mixture, and completed at 100° . The compound is a colourless liquid, boiling at $101-102^{\circ}/5$ mm.:

0.2163 gave 0.6095 BaSO_4 . $\text{S}=38.7$.

$\text{C}_6\text{H}_{12}\text{OS}_2$ requires $\text{S}=39.0$ per cent.

s-Diethylthioethane, $\text{SEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SEt}$, prepared by the action of ethylene dibromide on sodium ethylmercaptide at 100° , is a colourless liquid, boiling at 210° (Ewerlöf, *Ber.*, 1871, 4, 717; Meyer, *Ber.*, 1886, 19, 3266).

Phenyl mercaptan was obtained from Kahlbaum, and thiocarbonyl chloride from Schuchardt; both were purified by distillation. Diphenyl disulphide was prepared and purified by repeated crystallisation until quite colourless.

We are indebted to Professor Pope for a specimen of pure benzyl sulphide.

Carbonates.

An examination of the absorption curves (Figs. 1 and 2) shows that well-marked bands are exhibited by diethyl ditbio- and tritbio-carbonates ($M/1000$ -solutions), a less pronounced band by diethyl thioncarbonate ($M/100$ -solution) and by diphenyl carbonate and ditbiocarbonate ($M/1000$ -solutions), and by diphenyl thion- and tritbio-carbonates ($M/10,000$ -solutions). Table I gives the limits of general absorption in oscillation frequencies at a thickness of 30 mm., and, when stated, also at 2 mm.; the position of the head of the absorption band, when one is present, is also given.

TABLE I.

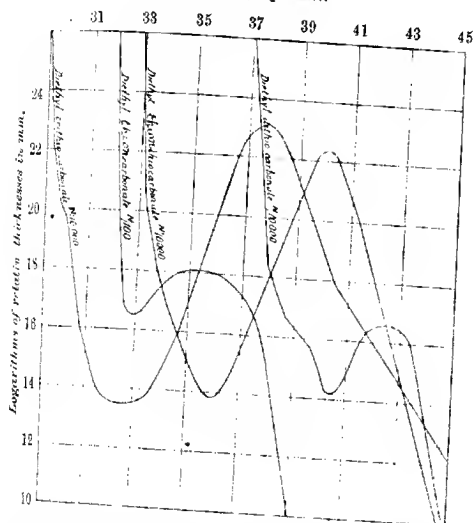
| Substance. | Strength of solution. | Head of band. | Limit of absorption. |
|--|---|---------------|----------------------|
| $\text{CO}(\text{OEt})_2$ (colourless) | $\left\{ \begin{array}{l} M/10 \\ M/10 \text{ (2 mm.)} \end{array} \right.$ | — | 4406 |
| $\text{CO}(\text{OPh})_2$ „ | $M/100$ | — | 4620 |
| $\text{CO}(\text{OPh})_2$ „ | $M/1000$ | 3760 | 3575 |
| $\text{CO}(\text{OEt})(\text{SEt})$ (colourless) ... | $\left\{ \begin{array}{l} M/10 \\ M/10 \text{ (2 mm.)} \end{array} \right.$ | — | 3435 |
| $\text{CO}(\text{OEt})(\text{SEt})$ „ | $M/1000$ | — | 4178 |
| $\text{CS}(\text{OEt})_2$ (yellow) | $\left\{ \begin{array}{l} M/10 \\ M/100 \end{array} \right.$ | — | 4254 |
| $\text{CS}(\text{OEt})_2$ „ | $M/1000$ | 3280 | 3047 |
| $\text{CS}(\text{OPh})_2$ (cream coloured) ... | $M/100$ | — | 3950 |
| $\text{CS}(\text{OPh})_2$ „ | $M/1000$ | — | 3336 |
| $\text{CO}(\text{SEt})_2$ (colourless) | $M/100$ | 3660 | 3453 |
| $\text{CO}(\text{SEt})_2$ „ | $M/10,000$ | — | 3513 |
| $\text{CO}(\text{SPh})_2$ „ | $M/1000$ | 4058 | 3722 |
| $\text{CS}(\text{OEt})(\text{SEt})$ (yellow) | $M/100$ | — | 3405 |
| $\text{CS}(\text{OEt})(\text{SEt})$ „ | $M/1000$ | 3600 | 3173 |
| $\text{CS}(\text{SEt})_2$ (orange) | $M/100$ | — | — |
| $\text{CS}(\text{SEt})_2$ „ | $M/10,000$ | 3260 | 2801 |
| $\text{CS}(\text{SPh})_2$ (golden-yellow)..... | $M/100$ | — | — |
| $\text{CS}(\text{SPh})_2$ „ | $M/10,000$ | 3300 | 2695 |
| CCl_2 (orange-red)..... | $\left\{ \begin{array}{l} M/10 \\ M/1000 \end{array} \right.$ | — | 3626 |
| | | | 3010 |
| | | | 3593 |

The results given above show that in general the replacement of an ethyl by a phenyl group causes a shift in the limit of general absorption towards the red end of the spectrum.

Further, the replacement of oxygen by sulphur in ethyl carbonate and ethyl thioncarbonate causes a very marked increase in the absorption.

The consideration of the cause of the colour and bands exhibited by these compounds is complicated by the differences which exist between the ethyl and phenyl esters. Diethyl carbonate shows

FIG. 1.
Oscillation frequencies.



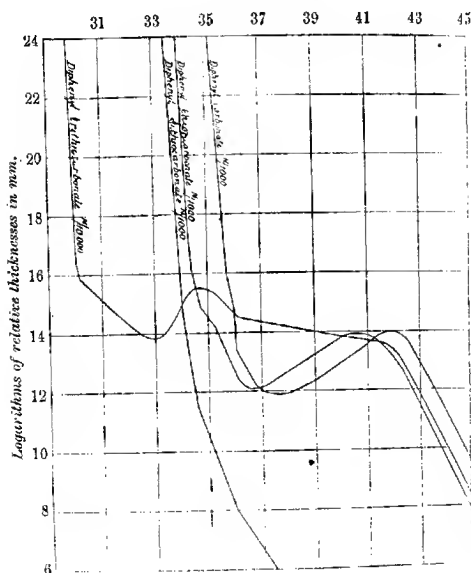
ely general absorption but no band, whilst diphenyl carbonate shows a well defined band (Fig. 2), with its head about 3740, oscillation frequency) almost identical in position with that of enol. This band may therefore be attributed to the presence of the phenyl groups, the group $\text{O}:\text{C} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ having no tendency to produce band. This is the only case in which the modification of the ure by the substitution of phenyl for ethyl is in the direction of band formation; usually a band shown by the ethyl ester is partly and completely obliterated in the phenyl ester, as, for instance, in a dithiocarbonate and in the dithio-oxalate, which will be discussed

later. In the compound $\text{CS}(\text{OPh})_2$, the band shown by diphenyl carbonate has been displaced slightly towards the red end of the spectrum, whilst in diphenyl trithiocarbonate the band is so changed that its form suggests a compromise between the vibration due to the phenyl groups, and those due to the group $\text{S}:\text{C} \begin{smallmatrix} \text{S}^+ \\ \text{S}^- \end{smallmatrix}$, which produce the band found in diethyl trithiocarbonate.

In consequence of these complications introduced by the presence

FIG. 2.

Oscillation frequencies.



of phenyl groups, the curves of the ethyl esters only can be considered completely comparable with one another. Considering first the phenomenon of colour, it is obvious that the mere replacement of one or two oxygen atoms by sulphur does not give rise to colour, since diethyl and diphenyl dithiocarbonates are colourless; but it is also clear that the group :C:S must be regarded as a powerful chromophore.

The following compounds all exhibit colour which may be regarded as caused primarily by the :C:S group: CSCl_2 (orange-red), $\text{CS}(\text{OEt})_2$

(yellow), CS(OPh)_2 (cream), thiobenzophenone, CS(Ph)_2 (blue). In the case of thiobenzophenone and dimethoxythiobenzophenone, we have confirmed the results obtained by Gattermann (*Ber.*, 1895, **28**, 2868) as regards the properties of the compounds and the fact that their molecular weights in solution are normal. We have also been able to prepare these compounds by the interaction of dry silver sulphide and the corresponding chloride. The colour originating in the :C:S group is very considerably modified by the group to which it is attached, since in the cases mentioned above it varies from deep blue to cream.

The difference between the intensity of the colour exhibited by the compounds CS(OEt)_2 and CS(OPh)_2 is much more marked than that between diacetyl and benzil, but the explanation is possibly similar to that suggested by Baly and Stewart (*Trans.*, 1906, **89**, 502) to meet the case of these substances.

Until there is more exact knowledge as to the relation between the absorption of light and the structure of organic compounds, it is not desirable to formulate further hypotheses, but the striking difference between the groups :C:S and :C:O may be explained as suggested by Hewitt at the International Congress of Applied Chemistry, 1909, on the following consideration. The attraction between carbon and sulphur is less than that between carbon and oxygen, as evidenced by the ease with which the sulphur is replaced by oxygen in the thioketones, thioncarbonates, and thiocarbamides. The mass of the sulphur atom to be held by the smaller force of attraction is greater, and consequently the period of any vibration set up would be slower.

The bands exhibited by the three compounds CO(SET)_2 , CS(OEt)(SEt) , and CS(SEt)_2 possess a similar shape and persistency, but are shifted successively towards the red end of the spectrum, and become much broader. It is possible that these bands may arise owing to the formation of linkings between the sulphur atoms, which exhibit a greater tendency to become quadrivalent than does oxygen.

Oxalates.

Table II gives, for the oxalates and thio-oxalates, the strength of solution, position of head of band in oscillation frequency, and the limit of absorption through 30 mm. of solution.

Fig. 3 contains the curves for those substances which show bands.

TABLE II.

| Substance. | Strength of solution. | Head of band. | Limit of absorption. |
|---|-----------------------|---|----------------------|
| $(\text{CO}_2\text{Et})_2$ (colourless) | $M/10$ | — | 3513 |
| $(\text{CO}_2\text{Et})_2$ „ | $M/1000$ | — | 4123 |
| $(\text{CO}_2\text{Ph})_2$ „ | $M/100$ | Rapid extension of absorption between 3640 and 4000, indicating potential band. | 3490 |
| $(\text{CO}_2\text{Ph})_2$ „ | $M/10,000$ | | 3593 |
| $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{SEt}$ (almost colourless) | $M/10$ | — | 2770 |
| $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{SEt}$ „ | $M/1000$ | 3740 | 3520 |
| $(\text{CO}\cdot\text{SEt})_2$ (yellow) | $M/10$ | — | 2408 |
| $(\text{CO}\cdot\text{SEt})_2$ „ | $M/1000$ | 3640 | 3144 |
| $(\text{CO}\cdot\text{S}\cdot\text{C}_3\text{H}_7)_2$ „ | $M/10$ | — | 2484 |
| $(\text{CO}\cdot\text{S}\cdot\text{C}_3\text{H}_7)_2$ „ | $M/1000$ | 3620 | 3038 |
| $(\text{CO}\cdot\text{SPh})_2$ „ | $M/100$ | — | 2380 |
| $(\text{CO}\cdot\text{SPh})_2$ „ | $M/1000$ | Rapid extension of absorption between 3110 and 3850. | 3050 |

Table III gives similar data, including the limit of absorption for a thickness of 2 mm. of solution, for the thiomalonates and other compounds examined, which are all colourless, and none of which show bands.

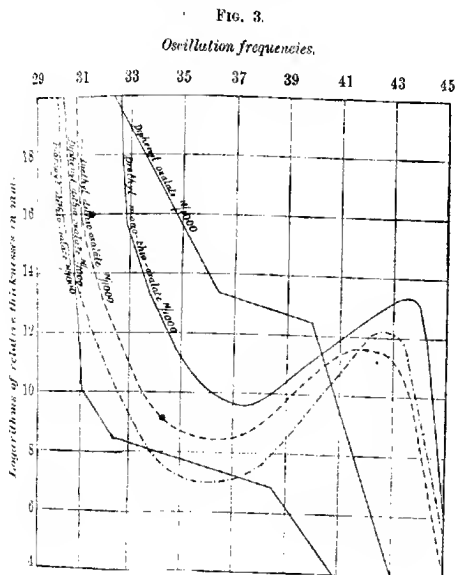
TABLE III.

| Substance. | Strength of solution. | Limit of absorption. |
|---|-----------------------|----------------------|
| $\text{CH}_2(\text{CO}\cdot\text{SEt})_2$ | $M/1000$ | 3727 |
| | $M/1000$ (2 mm.) | 4063 |
| $\text{CH}_2(\text{CO}\cdot\text{SPh})_2$ | $M/1000$ | 3405 |
| | $M/1000$ (2 mm.) | 4005 |
| $(\text{CH}_2\cdot\text{CO}\cdot\text{SEt})_2$ | $M/1000$ | 3855 |
| | $M/1000$ (2 mm.) | 4199 |
| $(\text{CH}_2\cdot\text{CO}\cdot\text{SPh})_2$ | $M/1000$ | 3447 |
| | $M/1000$ (2 mm.) | 4005 |
| $(\text{CH}_2\cdot\text{SEt})_2$ | $M/1000$ | 4365 |
| | $M/1000$ (2 mm.) | 4603 |
| $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ | $M/1000$ | 4351 |
| | $M/1000$ (2 mm.) | 4422 |
| $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{SEt}$ | $M/1000$ | 3330 |
| | $M/1000$ (2 mm.) | 4113 |

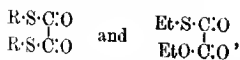
In all the above cases, the replacement of oxygen by sulphur produces a very great increase in the absorptive power of the compound; this is particularly well illustrated by a comparison of ethyl oxalate and monothio-oxalate (table II) and of the two last compounds in table III.

In the colourless compounds, the replacement of ethyl by phenyl produces a considerable increase in absorption, but this is not so marked in the coloured compounds, since in the dithio-oxalate the absorptive power of the phenyl compound is intermediate between those of the ethyl and propyl compounds.

The potential band exhibited by phenyl oxalate is probably due to the phenyl groups, as in the case of phenyl carbonate, since its position is close to that of the phenol band.



The table and the curves show that both colour and an absorption band are produced by the structures:



but when $\text{R}=\text{Ph}$ the band is almost obliterated, as in the case of the dithiocarbonate. Neither colour nor band is shown by any of the other compounds which were examined containing two atoms of sulphur in the molecule. It may therefore be concluded that the above structure is associated with the existence of the colour and the band.

Colour of Oxalyl Chloride in Solution.

It was observed that, although oxalyl chloride itself and its solutions in substances like ether, chloroform, and paraffins were quite colourless, yet it forms yellow solutions with phenol, anisole, piperonal, dipentene, and alkyl sulphides. The colour of these solutions is similar to, but deeper than, that of the alkyl dithio-oxalates, but the solutions were too unstable to allow of an examination of their spectra.

Oxalyl chloride therefore forms coloured solutions with certain substances which also give coloured solutions with tetranitromethane (Werner, *Ber.*, 1909, 42, 4324). The production of colour from oxalyl chloride by admixture with other substances is possibly due to the formation of additive products with these substances, which, in virtue of the presence of oxygen, sulphur, or ethenoid linkings in the molecule, are capable of forming such additive compounds.

Much further work will be required before definite hypotheses can be formulated to account for the behaviour of these sulphur compounds, and it is hoped that the study may be continued and possibly extended to some corresponding selenium compounds.

The absorption spectra of phenyl mercaptan and benzyl sulphide have also been examined for comparison with phenol and benzyl alcohol. These substances show no band, and the limits of absorption are given in table IV.

TABLE IV.

| Substance. | Strength of solution. | Limit of absorption. |
|-------------------------|-----------------------|----------------------|
| C_6H_5SH | $M/100$ (30 mm.) | 3320 |
| | $M/1000$ (30 mm.) | 3460 |
| $(C_6H_5CH_2)_2S$ | $M/100$ (30 mm.) | 3532 |
| | $M/1000$ (30 mm.) | 3608 |

It is remarkable that the pronounced band in phenol has been completely obliterated by the replacement of oxygen by sulphur, and that the three bands in benzyl alcohol (Baly and Collie, *Trans.* 1905, 87, 1332) have disappeared in benzyl sulphide.

The results obtained in the examination of benzyl mercaptan are not trustworthy on account of the ease with which it is oxidised in solution.

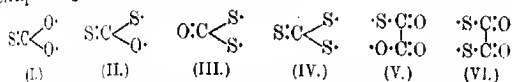
The obliteration of bands is possibly to be attributed to the greater absorptive power of the sulphur compounds.

General Results.

An examination of the absorption spectra of sulphur compounds has shown that:

(1) The replacement of oxygen by sulphur causes a marked increase in the absorptive power of the compound, and, indeed, often results in the production of colour. An absorption band also appears in some cases.

(2) Definite absorption bands are shown by sulphur compounds possessing the following structures, but are not shown by the corresponding oxygen compounds:



Of these, compounds of the type I, II, IV, and VI are yellow in colour, and V may be considered as faintly coloured.

(3) The group $\text{S} \cdot \text{C} <$ must be considered a powerful chromophore.

(4) In certain aromatic compounds, such as phenol and benzyl alcohol, the replacement of oxygen by sulphur results in obliterating absorption bands.

(5) It has also been found that, although oxalyl chloride itself is colourless, it gives yellow solutions with a number of unsaturated compounds and compounds containing oxygen or sulphur.

The expenses of this work were largely defrayed by grants from the Government Grant Committee of the Royal Society, and the spectra were examined by means of a spectroscope kindly placed at our disposal by the same body. For both these favours we are glad to make this grateful acknowledgment.

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CXIII.—*Phenomena Observed when Potassium Mercuri-iodide is Dissolved in Ether and Water.*

By JAMES ERNEST MARSH.

POTASSIUM mercuri-iodide, $\text{KHgI}_3 \cdot \text{H}_2\text{O}$, crystallises well from alcohol, but is decomposed by water with separation of mercuric iodide. A crystal of the salt changes in colour from yellow to red on being moistened with water. The salt is, however, soluble in water if heated with a very small quantity; also, when heated in

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a sealed tube, the dry salt melts at 119° , and this liquid may be regarded as a solution of the salt in its water of crystallisation. The salt is very sparingly soluble in dry ether, but is somewhat readily dissolved by undried ether, especially by ether which has been shaken with water and then separated from the latter. The salt, which dissolves in the ether with considerable rise of temperature, is much more soluble in cold ether than in hot. The following experiment illustrates this property. A sealed tube was employed containing 3.32 grams of powdered potassium iodide and 9.08 grams of mercuric iodide with 52 c.c. of "wet" ether and 0.6 c.c. of water. At 0° the contents of the tube are completely dissolved. If the tube is now placed in warm water, crystals begin to form, and at 50° the contents of the tube become nearly solid, with the formation of long, yellow needles of the salt $\text{KHgI}_3 \cdot \text{H}_2\text{O}$. The crystals redissolve in the ether on cooling. Analysis of the salt obtained in this way gave:

Found, $\text{H}_2\text{O} = 2.69$; $\text{KI} = 25.7$.

$\text{KHgI}_3 \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 2.82$; $\text{KI} = 26.0$ per cent.

If potassium iodide and mercuric iodide are mixed with ordinary undried ether, no apparent solution or other change occurs. The red and the colourless salts remain unchanged in presence of the solvent. After many weeks, however, the red colour of the mercuric iodide begins to fade, and its place is taken by the characteristic yellow, crystalline double salt. This does not dissolve appreciably in the ether now deprived of its water, but requires "wet" ether for its solution.

When potassium iodide and mercuric iodide are mixed with ether dried either by sodium or by long keeping over calcium chloride, the double salt which contains water of crystallisation cannot now be formed, and a quite different action occurs. The two salts rapidly liquefy in the ether, and take up four molecules of ether to form a heavy, yellow liquid compound. If any excess of ether is taken, it is left floating on the surface as a separate layer which contains very little of the salts, and a large excess of ether does not appreciably diminish or increase the volume of the liquid compound. If the ether taken is not enough to supply four molecules, then some of the salts are left undissolved. If mercuric iodide is taken in larger quantity than one molecule to one of potassium iodide, the excess is left undissolved.

The compound, $\text{KHgI}_3 \cdot 4\text{Et}_2\text{O}$.—1.66 Grams of well powdered and dried potassium iodide and 4.54 grams of mercuric iodide were mixed with 4.4 c.c. of dry ether in a sealed tube. On shaking, all rapidly passed into solution. The liquid compound measured 5 c.c., and the ethereal layer 0.1 c.c., at 7.5° . From these figures the

formula of the liquid compound and its specific gravity, 1.87, at 7.5° are derived. It should be noted that the solubility of potassium iodide and of mercuric iodide separately in dry ether is very slight. The solubility of potassium iodide in ether at the ordinary temperature was found to be 0.016 per cent., and of mercuric iodide 0.3 per cent., and in neither case is there formed any liquid not miscible with ether. The liquid compound of ether and potassium mercuri-iodide is also formed by exposing a mixture of the two salts in a tube to the vapour of ether, but in this case some crystals are also formed in the tube, and the action is very slow. 0.83 Gram (1 mol.) of potassium iodide and 2.27 grams (1 mol.) of mercuric iodide exposed to the vapour of dry ether increased in weight by 1.1682 grams (3.1 molecules of ether), when the red mercuric iodide just dissolved, and gave a further increase, in all 1.5334 grams (4.1 molecules of ether), after keeping for many days. The compound was also analysed by determining the loss of weight due to the ether given off on passing a stream of dry air over the substance. The liquid, when it had lost a certain quantity of ether, began to crystallise, and soon formed a solid mass of crystals. It was then weighed, and the stream of air was continued until all the ether was expelled. 4.2914 Grams of the liquid compound gave 3.7088 grams of crystals, and finally 2.6314 grams of potassium and mercuric iodides. These numbers agree with four molecules of ether in the liquid compound, and with 2.5 molecules in the crystalline compound. As it is difficult to stop when the crystals are just free from liquid, it appears more probable that the crystalline compound is represented by the formula $\text{KHgI}_3 \cdot 3\text{Et}_2\text{O}$.

When the liquid compound is exposed to moist air, crystals of the hydrated salt $\text{KHgI}_3 \cdot \text{H}_2\text{O}$ at once form on the sides of the tube. The addition of a small quantity of water causes the liquid to set to an almost solid mass of crystals with total expulsion of the ether. The experiment was carried out as follows.

In a tube, containing 1.83 grams of potassium iodide, 5.0 grams of mercuric iodide, and 5 c.c. of dry ether, was placed a sealed bulb containing 0.22 gram of water, and a small piece of glass rod. The tube was then sealed, and, on mixing carefully so as not to break the bulb, the liquid compound was obtained with a small surface layer of ether. The bulb was then broken by a jerk, and the tube quickly became filled with a mass of yellow crystals insoluble in the ether.

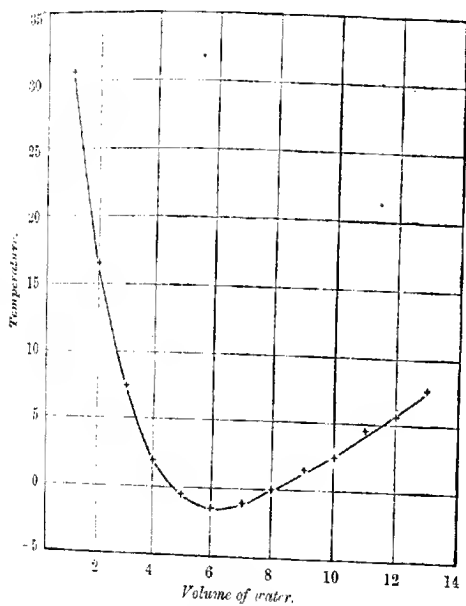
Solution of Potassium Iodide and Mercuric Iodide in a Mixture of Ether and Water.—As stated above, the addition of water to the compound $\text{KHgI}_3 \cdot 4\text{Et}_2\text{O}$ causes the precipitation of the salt $\text{KHgI}_3 \cdot \text{H}_2\text{O}$, and on the further addition of water the crystals

become soluble in aqueous ether, to separate again on warming the solution. By continuing the addition of water, these crystals no longer separate on warming, nor does the water cause the separation of ether, but eventually red mercuric iodide is precipitated. This occurs when the amount of water added is just double the volume of the ether; the addition of a little more ether clears the solution. With a larger amount of ether than four molecules to one of the salts, the addition of water may cause the liquid to separate into two layers. When there is separation, it is found that there is a temperature, the critical point, below which complete mixture takes place, and above which there is a separation into layers. This critical temperature depends on the concentration of the double salt in solution and the relative amounts of ether and water. It is to be noted further that, whereas the addition of water to the mixture of potassium and mercuric iodides brings about partial solution with absorption of heat, the addition of ether brings about complete solution with evolution of heat, and the further addition of the water to the aqueous ethereal solution also causes an evolution of heat. The following example shows the effect of increasing quantities of water, the amounts of potassium iodide, mercuric iodide, and ether being constant. One molecular proportion of potassium iodide and one of mercuric iodide were mixed with 12.5 molecular proportions of water; the temperature fell 2° , the solution not being complete. On addition of 12.5 molecular proportions of ether, the temperature rose 10° , the solution being now complete. The critical point of this solution was 31° . Successive additions of 12.5 molecular proportions of water were made, and a rise of temperature in each case was noticed until it became too small to be measured. The critical point was determined after each addition of water. The results are illustrated by the curve in Fig. 1. It will be seen that the critical point falls to a minimum and rises again. It was found that the solution of lowest critical point froze when the temperature was reduced to about -15° . The composition of the liquid of lowest critical point, and therefore also of the frozen mass, is represented nearly by the rather complex formula $\text{KHgI}_3 \cdot 12.5 \text{Et}_2\text{O} \cdot 75 \text{H}_2\text{O}$. The volume relations are more simple, being nearly 1 vol. KHgI_3 : 3 vols. Et_2O : 3 vols. H_2O . When partly melted and no longer adhering to the sides of the tube, the solid mass floats on the surface of the liquefied part.

There is a further point to be noted with regard to the critical point. It is found that, when the most concentrated solution, namely, that which has the critical point of 31° , is heated, a heavy liquid layer separates at the bottom of the tube, increasing in amount as the temperature rises, and being redissolved as the

temperature falls, until at 31° it disappears altogether. On the other hand, all the other solutions, when heated above their critical points, expel a light layer, which increases with the temperature and is re-absorbed by the bulk of the liquid just below the critical point. It will thus be seen that a solution of one molecular proportion of potassium mercuri-iodide in 12.5 molecular proportions of ether and 12.5 of water expels, on warming, a heavy liquid layer, whereas a solution containing the same quantities with an addition of 12.5 molecular proportions or more of water expels, on warming,

FIG. 1.



a light liquid layer. If, now, we take an intermediate amount of water, namely, 18.75 molecular proportions, the other quantities remaining the same, a solution is obtained which, on warming, expels both a heavy liquid layer and a light one, so that three different liquids appear in the tube. In one experiment a sealed tube was used which contained 5.53 grams of potassium iodide, 15.1 grams of mercuric iodide, 10 c.c. of water, and 44.2 c.c. of wet ether. This solution is homogeneous at the ordinary temperature, and between 50° and 60° a good separation is obtained

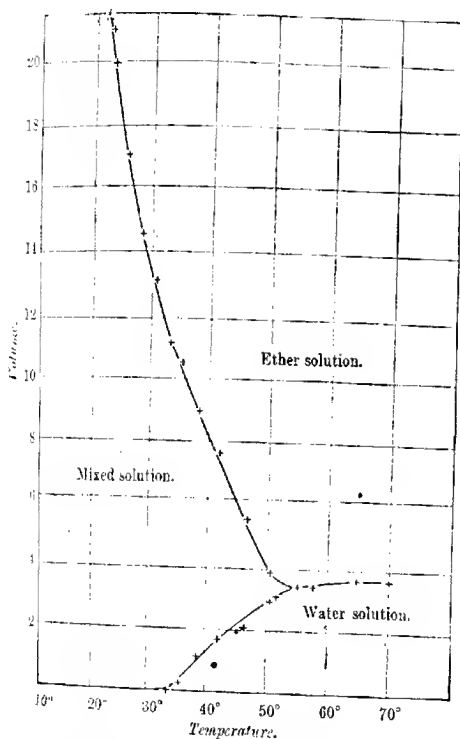
into three liquid layers. These layers are permanent and not altered by shaking while the liquid is still hot, but on cooling they form again a homogeneous solution.

It is possible to obtain other solutions which, on heating, give three liquid layers and have concentrations different from that just mentioned. The one which was first obtained contained equal molecular proportions of water and ether. As has already been stated, with the concentration of 1 to 12.5, a lower layer begins to separate at 31°; with the concentration of 1 molecular proportion of salt to 25 molecular proportions of ether and 25 of water, the upper layer separates above the critical point 0°. By trying concentrations between these two limits, it was found that with the concentration of 1 molecular proportion of potassium mercuri-iodide to 17.3 molecular proportions of water and 17.3 of ether, the solution separated into three layers. In a calibrated tube, 1.66 grams of potassium iodide, 4.54 grams of mercuric iodide, 2.6 c.c. of water, and 18.2 c.c. of "wet" ether were sealed. The calculated volume of the constituents is 22.0 c.c. The volume found on mixing was 21.4 c.c., so that there was a slight contraction. The tube was then heated to different temperatures, and the volumes of the solutions were determined. The curve plotted from the measurements is given in Fig. 2. In what follows, the top layer is termed "ether" solution, the middle layer "mixed" solution, and the lower layer "water" solution. At 22°, "ether" solution begins to separate, and increases in amount as the temperature rises. At 33.5°, "water" solution also begins to separate, and both layers increase with the temperature. At 51.5°, the "mixed" solution disappears, and only two liquids are present. These two liquids do not appreciably alter in volume on heating further to above 70°. Correction was made for expansion by heat which was regular, and nearly the same as the expansion of ether itself. In order to determine the amounts of mercuric iodide and potassium iodide in the water layer, a tube was taken with a bulb of 4 c.c. capacity at one end, the mixture in the tube being made up of 2 molecular proportions of potassium mercuri-iodide (12.1 grams) to 25 of ether and water. On heating, the heavy aqueous solution just filled the bulb at 63°. The tube was cooled without mixing the two solutions, opened, and the solutions separated. The aqueous solution measured slightly less than 4 c.c. The mixed salts contained in it weighed 4.77 grams, of which 1.58 grams was potassium iodide. The solution contained scarcely any ether, it did not take fire (water containing 0.5 per cent. of ether takes fire), and had scarcely any odour of ether. It was thus found that an aqueous-ethereal solution of the salts, which is homogeneous when

cold, separates, on warming, into a "water" solution nearly free from ether, and an "ether" solution which, from the volumes of the two solutions, can contain but little water.

In order to determine how the mercuric and potassium iodides are apportioned in all the three layers, a solution was made which gave three layers at a temperature below the boiling point of ether.

FIG. 2.



The three layers can then be produced in a stoppered burette, and run off and analysed. It was found that with 1 molecular proportion of salt to 20 molecular proportions of water and 33 of ether, separation into three layers is obtained at 29°. The "water" layer measured 0.6 c.c., had a concentration of 1 gram per c.c., and contained HgI_2 : $\text{KI} = 2:3$ mols. The "middle" layer measured

6.2 c.c., had a concentration of 0.4 gram per c.c., and contained HgI_2 : KI = 1: 1 mol. The "ether" layer measured 31 c.c., had a concentration of 0.1 gram per c.c., and contained HgI_2 : KI = 7: 6 mols.

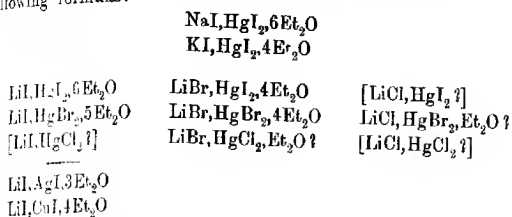
It will be noticed that the "water" solution contains more, and the "ether" solution less, potassium iodide than is represented by the simple molecular proportions HgI_2 : KI . It was found that "wet" ether will dissolve mercuric iodide and potassium iodide in any proportions between the lower limit KI : HgI_2 and the upper limit KI : 2HgI_2 . The upper limit of solubility of water is KI : HgI_2 , whilst there is, of course, no lower limit.

There seems no doubt that this separation of a homogeneous solution into layers on warming is associated with the temperature changes which occur on making the solutions. There are four operations, three of which occur with evolution of heat, and one with absorption of heat. In the first place, mercuric iodide and potassium iodide together dissolve in water with absorption of heat. The same salts dissolve in ether with evolution of heat, and ether dissolves in the "water" solution with evolution of heat, and water also dissolves in the "ether" solution of the salts with evolution of heat. It would be expected that the effect of raising the temperature would be to assist the change which occurs with absorption of heat, and to prevent those changes which occur with evolution of heat. Thus either ether will be expelled from solution, which happens at low concentrations, or water will be expelled, which happens at high concentrations, or both ether and water will be expelled, and further the salts will be expelled from the "ether" solution into the "water" solution. There is thus eventually produced, at a sufficiently high temperature, a strong aqueous solution, together with a weak ethereal solution of the two salts. These changes are reversed on cooling. If not shaken, however, the solutions may be kept apart when cooled; they mix then on shaking without change of temperature or volume. The great concentration of salts in the "water" layer is well shown by beating a tube, containing 1 molecular proportion of salt to 12.5 molecular proportions of water, to about 70° , and then, without shaking, cooling rapidly to 0° . The "water" layer now becomes filled with crystals of the double salt mixed with the red crystals of mercuric iodide.

Compounds of Two Haloid Salts with Ether.

A number of compounds analogous to the compound $\text{KHgI}_3 \cdot 4\text{Et}_2\text{O}$ were also prepared. The alkali-metal iodides form liquid compounds with mercuric iodide and ether, with the exception of

rubidium and cesium iodides. The compounds obtained have the following formulæ:



The compound $\text{KI, HgI}_2, 4\text{Et}_2\text{O}$ is described on p. 2298. The amount of ether (4 molecules) is approximately correct at the ordinary temperature, but the compound is affected by a rise of temperature with loss of some of the ether. This effect is found to be a general one for this class of substances even when they are contained in sealed tubes; it is small in the case of the lithium and sodium mercuri-iodides. The experiments which are now to be described are not therefore intended to furnish accurate analytical data, but rather to show how the substances were obtained. They indicate also that the constituents are combined at the ordinary temperature in approximately simple molecular proportions, the amount of the solvent being limited to six molecules or less. The liquids can, however, hardly be regarded as "definite" compounds in the ordinary sense, nor are they ordinary solutions, since they are saturated both for salt and for solvent. They seem to be of a nature intermediate between a solution and a chemical compound.

Compounds of Iodides with Mercuric Iodide and Ether.

Lithium Iodide.—Lithium iodide alone is readily soluble in dry ether, although not in undried and "wet" ether. It does not, however, form a liquid compound with a limited amount of ether in presence of excess of ether.

1.4 Grams of lithium iodide and 5.05 grams of mercuric iodide were mixed in a stoppered burette with 10 c.c. of dry ether, when all dissolved rapidly, forming two liquid layers. The volume of the solution was 8.15 c.c., and that of the upper ether layer 2.55 c.c. The latter left, on evaporation, 0.015 gram of solid residue, consisting of lithium mercuri-iodide, LiHgI_3 . Hence the liquid compound contained 1.387 grams of lithium iodide, 5.038 grams of mercuric iodide, and 7.45 c.c. of ether in 8.15 c.c. From these numbers is derived the formula $\text{LiI, HgI}_2, 6\text{Et}_2\text{O}$, and the specific gravity 1.461.

Sodium Iodide.—1.53 Grams of sodium iodide and 3.67 grams of

mercuric iodide were sealed in a tube with 6 c.c. of dry ether. The contents of the tube liquefied readily on shaking, with the exception of some sodium iodide, of which excess was taken by accident. The ether not required was 0.8 c.c. The formula of the compound formed is $\text{NaI}, \text{HgI}_2, 6\text{Et}_2\text{O}$.

Rubidium Iodide.—Rubidium iodide and mercuric iodide in contact with dry ether gave no liquid compound. There is no apparent action at first, but after some days the red mercuric iodide disappears, and its place is taken by a yellow, crystalline substance.

Caesium Iodide.—Caesium iodide and mercuric iodide gave no liquid compound with ether, and after several months most of the mercuric iodide appeared to be unchanged.

Silver Iodide.—Silver iodide and mercuric iodide in ether do not appear to suffer any change.

Strontium Iodide.—1.44 Grams of strontium iodide and 3.67 grams of mercuric iodide, with 6 c.c. of dry ether, liquefied and combined with 2.63 c.c. of the ether; hence the formula of the liquid compound is $\text{SrI}_2, 2\text{HgI}_2, 6\text{Et}_2\text{O}$.

Aluminium Iodide.—Aluminium iodide and mercuric iodide did not give any liquid compound with ether, but the colour of the mercuric iodide disappeared with the formation of a yellow precipitate and, after a time, of large, colourless crystals.

Hydrogen Iodide.—1.27 Grams of mercuric iodide were mixed with 3 c.c. of dry ether, and dry hydrogen iodide was passed in until the mercuric iodide just dissolved. Two layers of liquid were formed, and the upper layer of unused ether measured 2.25 c.c. The probable formula of the compound is $\text{HI}, \text{HgI}_2, 3\text{Et}_2\text{O}$.

Tetramethylammonium Iodide.—Tetramethylammonium iodide and mercuric iodide suffer no apparent change in dry ether after several months.

Ammonium Iodide.—The compound of ammonium iodide and mercuric iodide with ether differs from the other compounds described, in that its composition is different at different temperatures. 0.584 Gram of ammonium iodide and 1.83 grams of mercuric iodide, with 3 c.c. of dry ether, gave two liquids, the unused ether measuring 0.8 c.c. This agrees with the formula $\text{NH}_4\text{I}, \text{HgI}_2, 5\text{Et}_2\text{O}$. At about 80° , 1 molecule of ether is expelled from the lower to the upper layer in the sealed tube. Thus the compound $\text{NH}_4\text{I}, \text{HgI}_2, 4\text{Et}_2\text{O}$ is left.

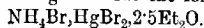
If water is added to ammonium and mercuric iodides dissolved in excess of ether, no crystalline hydrate separates, but the water is absorbed to a certain amount, and then any excess of water remains undissolved as a light layer floating on the heavy ether solution. The water layer contains very little of the salt dissolved.

Compounds of Bromides with Mercuric Bromide and Ether.

Lithium Bromide.—0.4 Gram of lithium bromide and 1.8 grams of mercuric bromide were sealed in a tube with 3 c.c. of dry ether. The mixture readily liquefied, and formed two layers. The amount of ether in excess was 1.02 c.c., hence the formula of the liquid compound is $\text{LiBr}, \text{HgBr}_2, 4\text{Et}_2\text{O}$.

Sodium Bromide.—Sodium bromide and mercuric bromide gave no liquid compound with ether.

Ammonium Bromide.—1.43 Grams of ammonium bromide and 5.3 grams of mercuric bromide were sealed in a tube with 5.5 c.c. of ether. The salts liquefied, but not quite completely, and required 3.66 c.c. of ether. This agrees with the formula



This compound, however, like the corresponding iodide, loses ether when warmed in the sealed tube, leaving not another liquid compound, but a solid mass, with loss of probably all the ether. The mass slowly unites again with the ether when cold. Further, when the liquid compound itself is cooled to about 10° , it sets to a solid mass of colourless crystals without any loss of ether.

Lithium Chloride and Mercuric Chloride.

0.42 Gram of lithium chloride and 2.71 grams of mercuric chloride were sealed with 3 c.c. of dry ether in a tube. No liquid compound was obtained, but, on long keeping, crystals formed in the tube.

Mixed Halogen Salts and Ether.

Lithium Bromide, Mercuric Iodide, and Ether.—0.45 Gram of lithium bromide and 2.27 grams of mercuric iodide were mixed with 3 c.c. of dry ether in a sealed tube. The salts liquefied, taking up 2.15 c.c. of ether. From these numbers the formula $\text{LiBr}, \text{HgI}_2, 4\text{Et}_2\text{O}$ is derived.

Lithium Iodide, Mercuric Bromide, and Ether.—0.76 Gram of lithium iodide and 2.15 grams of mercuric bromide liquefied in contact with 4 c.c. of dry ether, and required 3.14 c.c. for solution; hence the formula of the compound is $\text{LiI}, \text{HgBr}_2, 5\text{Et}_2\text{O}$. Neither lithium chloride with mercuric iodide nor lithium iodide with mercuric chloride gave any liquid compound with ether.

Lithium Bromide, Mercuric Chloride, and Ether.—0.85 Gram of lithium bromide and 2.65 grams of mercuric chloride were mixed with 4 c.c. of dry ether. The action was slow and did not appear complete, but partial liquefaction occurred. The amount of ether taken up was 1.06 c.c.; hence the probable formula of the compound is $\text{LiBr}, \text{HgCl}_2, \text{Et}_2\text{O}$.

Lithium Chloride, Mercuric Bromide, and Ether.—0.21 Gram of lithium chloride and 1.8 grams of mercuric bromide became paste in contact with 2 c.c. of dry ether without completely liquefying. The amount of ether taken up was 0.7 c.c.; hence the probable formula of the compound is $\text{LiCl}, \text{HgBr}_2, \text{Et}_2\text{O}$.

All the liquid compounds with ether mentioned above contain a mercury salt as one constituent. The following are examples of liquid ether compounds, where silver, lead, and copper iodides take the place of mercury salts.

Lithium Iodide, Silver Iodide, and Ether.—1.82 Grams of lithium iodide and 2.67 grams of silver iodide were sealed with 6 c.c. of dry ether in a tube. Liquefaction took place rapidly, two layers were formed, and 3.6 c.c. of ether were taken up. From this the formula $\text{LiI}, \text{AgI}, 3\text{Et}_2\text{O}$ is deduced.

Lithium Iodide, Copper Iodide, and Ether.—1.45 Grams of lithium iodide and 2.05 grams of cuprous iodide were sealed in a tube with 5 c.c. of dry ether. A liquid compound was obtained, but was not clear. The ether not used was 0.85 c.c. Hence the probable formula of the compound is $\text{LiI}, \text{CuI}, 4\text{Et}_2\text{O}$.

Lithium Iodide, Lead Iodide, and Ether.—0.87 Gram of lithium iodide and 2.62 grams of lead iodide were sealed in a tube with 4 c.c. of dry ether. Ether was absorbed, and the compound formed was solid and crystalline. It melted partly on warming, but a clear liquid was not formed. The composition is doubtful; apparently between 3 and 4 molecules of ether are required.

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CCXLII.—*The Relation between the Crystal Structure and the Chemical Composition, Constitution, and Configuration of Organic Substances.*

By WILLIAM BARLOW and WILLIAM JACKSON POPE.

DURING the last few years the authors have investigated a novel method of studying the relations between crystalline and molecular structure, and have demonstrated the existence of a very simple relation between the two species of structure in a great variety of cases (Trans., 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528); the principles involved in the method referred to were briefly summarised in the introduction of the last-mentioned communication. One of the chief results of this work has been to demonstrate

that, in a given crystalline substance, the volumes appropriated by the spheres of influence of the different atoms contained in the molecule are approximately proportional to the numbers representing the respective fundamental valencies; this conclusion has been independently verified for hydrocarbons and their simple derivatives containing oxygen or nitrogen in the liquid state by Le Bas (*Trans.*, 1907, **91**, 112; *Phil. Mag.*, 1907, [vi], **14**, 324; 1908, **16**, 60). The latter author, indeed, carries the valency law a step further by showing that throughout a series of liquid hydrocarbons, under corresponding conditions, the atomic volumes are directly proportional to the numbers representing the fundamental valencies of the elements carbon and hydrogen.

In view of the close relation which has been shown to exist between the sum of the fundamental valencies of the atoms composing the molecule—the valency volume—and the crystalline structure affected by the substance, it is convenient to derive constants for related series of substances which are simple functions of the valency volume and of the crystalline structure as expressed by the geometrical data. We have therefore introduced the so-called "equivalence parameters," x , y , and z , which are the lengths of the edges of a parallelepipedon, of which the volume is the valency volume, V , and of which the relative linear and angular dimensions accord with the axial ratios and the interaxial angles (*Trans.*, 1906, **89**, 1681); the equivalence parameters are calculated as follows:

$$x = \sqrt{\frac{3}{c \sin A \sin \beta \sin \gamma}} \frac{a^2 V}{c}, \quad y = x/a \text{ and } z = cy.$$

The important nature of the information to be obtained by the aid of the equivalence parameters has been fully demonstrated in our previous papers, and by Jaeger (*Trans.*, 1908, **93**, 517), Jerusalem (*Trans.*, 1909, **95**, 1275), and Armstrong (this vol., p. 1578).

In the present paper we propose to discuss the close-packed assemblages representing the molecular composition, constitution, and configuration of the paraffinoid, ethylenic, and acetylenic hydrocarbons. As a result of this investigation we shall be able to show that, adopting the same principles as have been previously laid down, each hydrocarbon has its own specific kind of structural unit, and that geometrical peculiarities are distinguishable in the appropriate assemblages corresponding with the presence in the molecule of single, double, and triple bonds between carbon atoms. It will further be shown that the configurations derived for the various hydrocarbons by closely packing spheres of magnitudes appropriate for representing the spheres of influence of their atoms are in accordance with the conclusions of van't Hoff and Le Bel.

concerning the environment of a methane carbon atom. Finally, it will be shown that a process of simple adjustment furnishes a geometrical interpretation of polymerisation and isomeric change, such, for instance, as the conversion of acetylene into benzene. As a preliminary to the main argument, and in justification of the methods employed, a passing reference may be made to one or two simple considerations and the data supporting them.

Concerning the legitimacy of attributing to carbon a sphere of atomic influence four times as large as that of hydrogen, little more now remains to be said. Since we first drew this conclusion, Le Bas has conclusively proved the atomic volume of carbon to be four times that of hydrogen, and Jerusalem has shown the same relation to hold approximately as between crystalline substances which are not examined under strictly corresponding conditions. Most of the hydrocarbons of the series with which we have now to deal are, however, either liquid or gaseous under ordinary conditions, and therefore yield no crystallographic data for employment as a direct experimental check. For our present purpose it is consequently necessary to use crystallographic data referring to the halogen derivatives of hydrocarbons, and to rely on them to furnish the necessary check on the dimensions of the hydrocarbon assemblages described. The legitimacy of the use of these derivatives for this purpose depends on our previous conclusion that the spheres of atomic influence of hydrogen and the halogens differ but slightly in volume when contained in the same molecular complex (Trans., 1906, **89**, 1679), although the sphere of atomic influence of hydrogen is somewhat smaller than those of the halogens (Trans., 1907, **91**, 1197). That the spheres of atomic influence of hydrogen and the halogens have approximately the same valency volume may be conveniently demonstrated by showing that the chemical substitution of a halogen atom for one of hydrogen in a crystalline substance is frequently not accompanied by a profound change in axial dimensions; in the instances quoted below, it will be seen that the geometrical change accompanying the substitution in question is in general greater than that ordinarily observed in cases of isomorphism, but not so great as to obscure the obvious morphotropic relationship. The comparatively large change in axial dimensions which is in general thus presented, and also the rarity of such instances, must be attributed to the sphere of atomic influence of hydrogen differing appreciably in magnitude from those of chlorine, bromine, or iodine, the latter being much more nearly of the same size; the discrepancy in volume between the spheres of hydrogen and of the halogens is, however, not sufficient to necessitate the employment of different sizes of spheres of influence for those

elements in the construction of the close-packed assemblages described below.

The substitution of hydrogen by bromine, unaccompanied by considerable changes in axial dimensions, is illustrated by the data for the monosymmetric pentabromoethane and the orthorhombic hexabromoethane (Trans, 1906, 89, 1682):

| | |
|---|--|
| $\text{C}_2\text{H}_3\text{Br}_5$ | $a : b : c = 0.5650 : 1 : 0.3118 ; \beta = 91^\circ 19'$ |
| C_2Br_6 | $a : b : c = 0.5639 : 1 : 0.3142 ; \beta = 90^\circ$ |

A similar case is presented by the orthorhombic π -sulphonyl chlorides and bromides of camphor and of α -bromo- and α -chloro-camphor (Kipping and Pope, Trans., 1893, 63, 548; 1895, 67, 367):

| | |
|--|-----------------------------------|
| $\text{C}_{10}\text{H}_{16}\text{O}_2\text{SO}_2\text{Cl}$ | $a : b : c = 0.9950 : 1 : 1.0363$ |
| $\text{C}_{10}\text{H}_{16}\text{O}_2\text{SO}_2\text{Br}$ | $a : b : c = 0.9816 : 1 : 1.0249$ |
| $\text{C}_{10}\text{H}_{15}\text{OBrSO}_2\text{Cl}$ | $a : b : c = 0.8012 : 1 : 1.0518$ |
| $\text{C}_{10}\text{H}_{15}\text{OClSO}_2\text{Br}$ | $a : b : c = 0.8795 : 1 : 1.0494$ |

The axial dimensions of the monosymmetric *p*-azoxytoluene and its monobromo derivative are almost identical (v. Zepharovitch, *Zeitsch. Kryst. Min.*, 1889, 15, 214), and a similar relationship holds between the values for the orthorhombic *p*-tolyl-mono- and -bichloro-methylsulphones (Brugnatelli, *Zeitsch. Kryst. Min.*, 1892, 10, 601—603):

| | |
|--|---|
| <i>p</i> -Azoxytoluene..... | $a : b : c = 1.4971 : 1 : 1.0196 ; \beta = 75^\circ 39'$ |
| <i>p</i> -Bromo- <i>p</i> -azoxytoluene..... | $a : b : c = 1.5194 : 1 : 1.01 ; \beta = 75^\circ 28' 36''$ |
| Tetra-mono-chloromethylsulphone..... | $a : b : c = 0.9070 : 1 : 0.7865$ |
| Tetra-bis-bromomethylsulphone..... | $a : b : c = 0.8321 : 1 : 0.7912$ |

Acetamide is rhombohedral with $a : c = 1 : 0.5916$ (Kahrs, *Zeitsch. Kryst. Min.*, 1905, 40, 476); on referring the substance to rectangular axes by changing the indices $\{100\}$, $\{101\}$ and $\{110\}$ to $\{110\}$, $\{301\}$ and $\{301\}$ respectively, the values are obtained as:

$$a : b : c = 1.6904 : 1 : 0.9759 ; \beta = 90^\circ.$$

Dibromoacetamide is monosymmetric with $a : b : c = 1.6887 : 1 : 1.2785$, $\beta = 87^\circ 2'$ (Fock, *Zeitsch. Kryst. Min.*, 1888, 14, 358); when the transposition involved in changing the indices of $\{203\}$ to $\{101\}$ is made, the axial ratios are obtained as $a : b : c = 1.9887 : 1 : 0.8625$, $\beta = 87^\circ 2'$. The change of indices here made is legitimate, because the form $\{203\}$ is actually observed. Tribromo- and trichloroacetamide are also monosymmetric, and exhibit the axial ratios $a : b : c = 1.7339 : 1 : 0.8636$, $\beta = 79^\circ 37'$, and $1.7455 : 1 : 0.8490$, $\beta = 78^\circ 36'$ respectively. The four sets of axial ratios show a fairly close agreement.

The orthorhombic monochloro-*p*-benzoquinone exhibits the axial ratios, $a : b : c = 1.7461 : 1 : 0.9619$ (Fels, *Zeitsch. Kryst. Min.*, 1903, 37, 479); these ratios, expressed in the form $b : c : a =$

1.0396: 1: 1.8153, closely approximate to those of the monosymmetric dichloro-*p*-benzoquinone (Fock, *Zeitsch. Kryst. Min.*, 1883, 7, 40), namely, $a:b:c=1.0920:1:1.8354$, $\beta=89^\circ 11'$, and dibromo-*p*-benzoquinone (Fels, *loc. cit.*), which exhibit $a:b:c=1.0941:1:1.8229$, $\beta=92^\circ 32'$. The three substances are, however, pseudo-hexagonal, and the morphotropic relation between them is probably even closer than is indicated by the above axial ratios. Thus, on changing the forms $\{10\bar{1}\}$, $\{101\}$, $\{100\}$, and $\{103\}$ observed on dibromo-*p*-benzoquinone to $\{001\}$, $\{101\}$, $\{103\}$, and $\{100\}$ respectively, the axial ratios become $a:b:c=1.7416:1:0.9491$, $\beta=90^\circ 41'$. These values approximate much more closely to the original ones given above for monochloro-*p*-benzoquinone than do those stated by Fels. It is in any case clear that, contrary to the views of Grünling (*Zeitsch. Kryst. Min.*, 1883, 7, 582) and of Fels, very little change in axial dimensions attends the passage from monochloro-*p*-benzoquinone to dichloro- or dibromo-*p*-benzoquinone.

In the instances quoted above, the replacement of hydrogen by a halogen atom leads to no very profound change in crystallographic dimensions. The same kind of relation as is thus expressed must be looked for amongst halogen derivatives which are position isomerides, and several instances from amongst such substances may next be quoted.

The di- and tri-halogen derivatives of camphor have been very completely examined by (1) v. Zepharovitch (*Zeitsch. Kryst. Min.*, 1883, 7, 588), (2) Cazeneuve and Morel (*ibid.*, 1888, 14, 267), (3) Kipping and Pope (*Trans.*, 1895, 67, 371), and (4) Armstrong and Lowry (*ibid.*, 1898, 73, 579). The close morphotropic relationship between these orthorhombic substances becomes evident on interchanging the dimensions b and c in the data (1) and (2), dividing dimension b by two and writing b for a , c for b , and a for c in the data (3), and leaving data (4) as stated by Armstrong and Lowry; the following values are thus obtained:

| | Original. $a:b:c$ | Transposed. $a:b:c$ |
|---|----------------------|------------------------|
| (1) <i>aa</i> -Dibromocamphor | 0.7925 : 1 : 0.5143 | 1.5409 : 1 : 1.9943 |
| (2) <i>aa</i> -Dichlorocamphor | 0.8074 : 1 : 0.5448 | 1.4830 : 1 : 1.8365 |
| <i>aa</i> -Bromochlorocamphor | 0.8040 : 1 : 0.5228 | 1.5379 : 1 : 1.8355 |
| (3) <i>ax</i> -Dichlorocamphor | 0.6933 : 1 : 0.3297 | 1.5160 : 1 : 2.1029 |
| <i>ax</i> -Dibromocamphor | 0.6860 : 1 : 0.3323 | 1.5148 : 1 : 2.0886 |
| <i>ax</i> -Chlorobromocamphor | 0.6884 : 1 : 0.3301 | 1.5074 : 1 : 2.0642 |
| <i>ax</i> -Bromochlorocamphor | 0.6861 : 1 : 0.3317 | 1.5045 : 1 : 2.0654 |
| (4) <i>aa</i> -Chlorobromocamphor | 1.5338 : 1 : 1.9020 | 1.5333 : 1 : 1.9020 |
| <i>aa</i> -Dibromochlorocamphor ... | 1.4627 : 1 : 2.1332 | 1.4622 : 1 : 2.1332 |

Jaeger has shown (*Zeitsch. Kryst. Min.*, 1904, 38, 570) that the monosymmetric position isomerides, the 1:2:4- and the 1:3:4-tri-

bromotoluenes, have almost identical axial ratios, namely, $a : b : c = 3.5283 : 1.41958$, $\beta = 58^\circ 47'$, and $a : b : c = 3.5470 : 1.42603$, $\beta = 58^\circ 55'$, respectively.

A large number of instances similar to those quoted above might be selected from the crystallographic literature, but the above will suffice to confirm our previous conclusion that the sphere of atomic influence of hydrogen differs but slightly in volume from those of the halogen elements, and consequently that they are all represented in the close-packed, homogeneous assemblage with sufficient exactness by spheres of the same size. In the following pages we shall therefore assume that the crystallographic configuration of any hydrocarbon can be presented under some conditions by its halogen derivatives, and, when crystallographic data are available for any of the latter, shall directly employ those data for checking the correctness of the assemblage derived for the hydrocarbon itself. In connexion with the concluding portions of this communication, in which the occurrence of polymerisation and isomeric change is treated, it may possibly be suggested that no method of discussion involving considerations connected with crystal structure can be justified, inasmuch as such changes occur in general in the liquid or even in the gaseous state. To this objection the reply is made that the great mass of work done during recent years on so-called liquid crystals has greatly extended the domain of crystal structure. It is now known that in those liquid substances which exist in the liquid crystalline condition, tracts, so large as to be readily discerned microscopically, exist in which the regularity of arrangement exhibited by solid, crystalline structures is present. These tracts are continually forming and disappearing, and their occurrence indicates clearly that in these mobile liquids the particles aggregate themselves together in masses which, measured on a molecular scale, are of enormous extent, and in which very complete regularity of structure prevails. Since, in such instances as these, the eye can discern the existence of a liquid, crystalline structure, it is legitimate to assume that in liquids generally, arrangements of parts, comparable in regularity with crystalline structures, are being continually formed and dissolved, although possibly not to such an extent as in the cases of known liquid crystals. The occasional juxtaposition of parts in orderly close-packed arrangement thus premised is all that is required to legitimise the discussion of isomeric change in connexion with crystalline structure.

Methane.

As a preliminary to an attempt to apply the methods which we have previously described to the elucidation of the configurations

and properties of the paraffins, it is necessary briefly to enumerate the available chemical and crystallographic facts and conclusions bearing on the configuration of the simplest paraffin, methane. The following may be quoted as sufficient to lead to the construction of the homogeneous close-packed assemblage of spheres which represents this hydrocarbon.

(1) In accordance with the conclusions respecting valency which we have previously drawn (Trans., 1906, **89**, 1723), the space appropriated in the methane assemblage by each carbon atom should be four times as large as that appropriated by each hydrogen atom.

(2) Carbon tetrabromide, CBr_4 , possesses the same configuration as methane, and its assemblage will be represented by the same spheres. The halogen derivative is dimorphous, crystallising above 47° in the cubic system (Rothmund, *Zeitsch. physikal. Chem.*, 1897, **24**, 712) and at the ordinary temperature in the monosymmetric system. Carbon tetrachloride and tetraiodide crystallise in the cubic system.

(3) Stereochemical facts indicate that in the free methane molecule the four hydrogen atoms are situated at the apices of a regular tetrahedron described about the carbon atom, and that this tetrahedral environment of the methane carbon atom must be regarded as surviving a substitution of one or more of the four hydrogen atoms by other atoms or radicals.

(4) The assemblage representing methane, built up in accordance with the principles laid down in previous papers, should be capable of geometrical modification so as to yield assemblages representing other paraffins; the geometrical process thus involved should be strictly illustrative of the practical methods by which methane can be converted into these homologous paraffins. It should thus be possible to derive one assemblage corresponding in composition, constitution, and configuration with each paraffinoid hydrocarbon. An extension of the same method should lead to the derivation of characteristic assemblages for other aliphatic hydrocarbons and compounds other than the paraffins; the applications should embrace all the varieties of isomerism, and express the facts that have led to the conception of the asymmetric carbon atom.

An assemblage which, both as a whole and when partitioned, fulfils the above and other conditions concerning methane is arrived at in the following manner. Alternate layers are removed from a cubic closest-packed assemblage of equal incompressible but deformable spheres (Trans., 1907, **91**, 1152), regarded as composed of layers of square arrangement (Fig. 1), the remaining layers being caused to retain their original positions. The resulting skeleton assemblage, which has tetragonal symmetry, is shown in plan and

deviation in Figs. 2 and 3; the dotted lines which join the centres of nearest spheres in the three principal directions outline a partitioning of space into equal right square prisms.

FIG. 1.

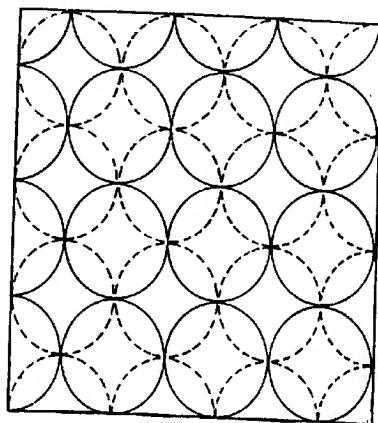
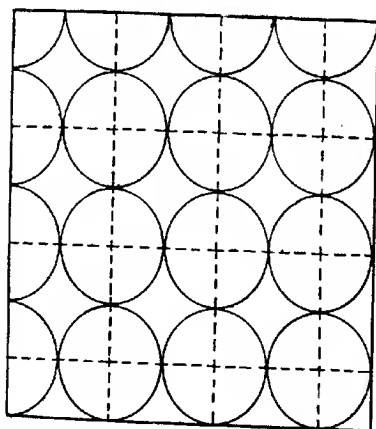


FIG. 2.



and one-fourth the volume of the original large ones, are forced into its cavities, and the whole system is then subjected to compression so as to eliminate the interstitial space, the polyhedra produced from the large spheres will be about four times as large as

those produced from the small ones. In the skeleton assemblage of Fig. 4, the cavities are as numerous as the spheres; if, therefore, each

FIG. 3.

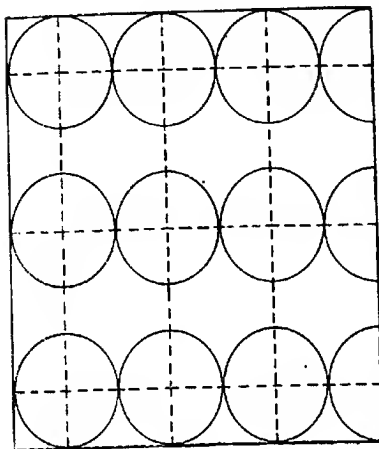
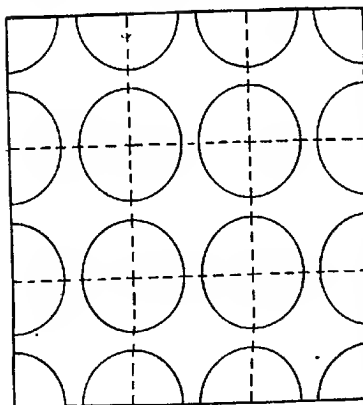


FIG. 4.



cavity bounded by eight neighbouring spheres can be made to accommodate a group of four of the small spheres in such a manner as to give stable equilibrium and to be compatible with cubic symmetry, several of the more essential conditions for methane will be obeyed by the assemblage.

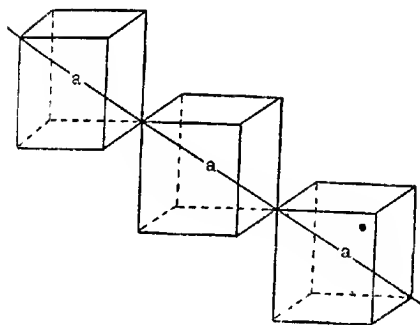
Each cavity of the skeleton assemblage described exhibits six identical four-sided hollows, the centres of which lie on three rectangular axes drawn through the centre of the cavity, and, in placing a tetrahedral group of the small spheres within the latter, any three of the hollows which lie nearest together are selected for the reception of three out of the four small spheres of the group, one jutting into each of the selected hollows. The fourth sphere of the tetrahedral group will then touch that

sphere of the eight of volume four which does not border either of the selected hollows, the point of contact being on the cube diagonal

which passes through the centre of this large sphere. The marshalling thus arrived at for a cubic unit of the assemblage is the one required; it has yet to be shown what relative orientations of the contents of the different cube cells are consistent with cubic symmetry and what adjustment of the arrangement described will restore the close-packing which has been impaired by substituting the tetrahedral groups of small spheres for one-half of the larger spheres of the closest-packed assemblage.

The introduction of the tetrahedral group into the cubic cell in the manner described lowers the symmetry by destroying three of the four trigonal axes of the cell; if cubic symmetry is to survive the introduction of such a tetrahedral group into each cavity, the arrangement of the completed assemblage must consequently be of one of the types in which the trigonal axes do not intersect. The

FIG. 5.

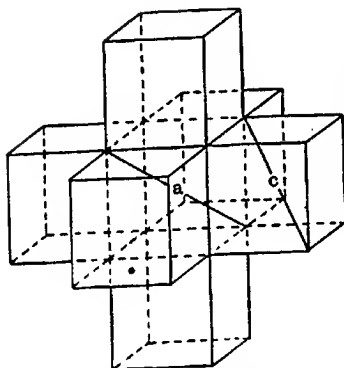


mode of ascertaining the relative positions of the non-intersecting trigonal axes has been already described (*Trans.*, 1907, **91**, 1183); its application to the present case leads, in the following manner, to the production of the appropriate type of symmetry for the methane assemblage.

In the cubic partitioning of space shown in Fig. 4, one trigonal axis, *a*, of one cube of the partitioning is drawn and produced in both directions, so as to pass through a string of cubic cells which are in contact at their corners (Fig. 5), the latter being centres of carbon spheres; in the first selected cube of the partitioning, the group of four small or hydrogen spheres is inserted in its appropriate position with respect to this trigonal axis. In any one of the six cubic cells which make face contact with the first selected cube cell, a single diagonal is drawn, the position chosen being such

that, like c in Fig. 6, it is not parallel to the trigonal axis a , already located and does not intersect it. This last drawn diagonal is used as a trigonal axis, and by rotations about it through 120° the existing trigonal axis and group of small spheres are transferred to two new positions, so as to locate other trigonal axes and groups of hydrogen spheres in the system. The latter process is repeated about the axes thus located and about subsequently located axes, until all the situations for trigonal axes in their four orientations and all the positions for groups of small spheres derivable in this manner have been ascertained; the minimum distance separating trigonal axes of different orientations is that separating the two first located. A diagram showing the relative situations of the axes has

FIG. 6.



been already given (Trans., 1907, 91, 1183).

As a result of this series of operations, one trigonal axis becomes located in each cube cell of the cubic partitioning of space, but the original tetrahedral group of small spheres becomes transferred to but one-half of these cube cells. The cube cells forming the half system, distinguished by each cell containing a tetrahedral group of small spheres, are in

contact at their edges only; they have the arrangement of the light or the dark cubes of the previously described stack of cubes of two kinds (Trans., 1908, 93, 1533, Fig. 1). The skeleton assemblage thus derived has the symmetry of Barlow's type 1.

Only one kind of arrangement possessing cubic symmetry can be arrived at in the manner just described, but there are two alternative ways in which to complete the assemblage homogeneously by filling the unoccupied cavities, which are equal in number to those occupied, with the tetrahedral groups of small spheres in a manner compatible with cubic symmetry; both of these involve slight adjustment of the skeleton assemblage, but no re-marshalling. The completion is in both cases effected by bringing the one-half system of cubes to the place of the other half system. One of the two alternative operations consists in rotating the system through 180°

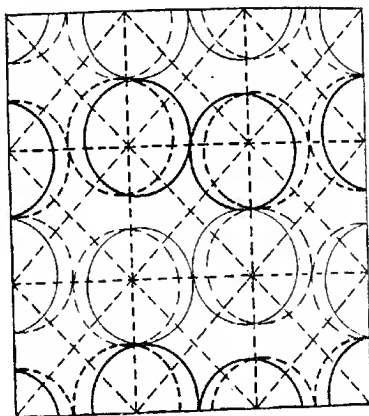
about an axis drawn perpendicular to a cube face and passing through the centre of a cube edge, such perpendicular not being a digonal screw axis of the skeleton assemblage; this involves the addition of digonal rotation axes to the original system of trigonal axes and digonal screw axes, and yields a completed assemblage having the symmetry of Barlow's type 2. The other operation is one performed about a centre of symmetry situated at a cube angle, and leads to the production of a completed assemblage having the symmetry of Barlow's type 1a (*Zeitsch. Kryst. Min.*, 1894, **23**, 10, 11). Both assemblages thus derived become very closely packed as the result of a slight adjustment, but the assemblage of type 2, which displays tetartohedral cubic symmetry, appears to be capable of modification of closer packing than the other. It is, moreover, the assemblage indicated by the facts as representing methane; each of the large spheres in it is similarly situated with respect to the groups of small spheres, whilst in the assemblage of type 1a the large spheres form two sets, the members of one of which differ in environment from those of the other. The latter type of assemblage probably has a practical application, although not in the present connexion.

With respect to the relative orientation of the tetrahedral groups of small spheres in the assemblage of type 2, it is to be noted that the groups contained within the one half set of the cubes of the partitioning are related by a simple operation, besides that of rotation about a digonal axis, to those contained within the other half set. The relation consists in the existence of four similar translations having the four directions of the sets of trigonal axes. Either of these operates to bring a cubic cell to the place of a neighbouring cubic cell, which is in contact with the first at one of its corners. In addition to being identical, the two half systems of cubes with their contained groups of four small spheres consequently have the same orientation, and the assemblage as a whole is hemimorphous, like the assemblage of type 1 from which it is derived.

It has been already noticed that in order to render the packing close, a modification or deformation of the whole assemblage must occur. The eight large or carbon spheres enclosing a single cavity may be regarded as forming six indivisible quartettes, one for each of the six faces of the cubic cell containing the cavity; the four spheres composing a quartette form two square hollows, one in each of its opposite faces, and these two hollows communicate with each other at the centre of the quartette. Where a small sphere occupies the hollow on one face, the existence of a digonal axis bisecting the cell face involves the presence of another small sphere in the hollow on the other face of the same quartette, and therefore one half of

the quartettes of large spheres in the assemblage are occupied, and the other half unoccupied, by the smaller spheres. It follows that some increase in the closeness of the packing will be likely to supervene if it is possible symmetrically to adjust the arrangement of the larger spheres, without altering the marshalling, in such a way as similarly to diminish the size of one-half of the hollows—the unoccupied ones—while slightly increasing the size of the rest—the occupied ones. Three of the six hollows present in each cavity, namely, the unoccupied ones, will in this event become contracted. Such an adjustment of the larger spheres, which does not alter the type of symmetry, consists in a slight equal shift of each large sphere along its trigonal axis in either direction; the choice made of

FIG. 7.



the direction of shift for any one sphere necessarily determines the directions for all if the assemblage is to remain compatible with the coincidence movements of type 2. The amount of shift is limited by the approximation of the large spheres, causing them to come into contact at points lying on the diagonal axes of rotation which characterise type 2. An important feature of the change is that the large or carbon spheres, in shifting, close in around that hydrogen sphere of each tetrahedral group the centre of which lies on the trigonal axis; the position of the tetrahedral groups undergoes slight adjustment during the process.

A projection of the resulting assemblage, showing the carbon spheres alone, is given in Fig. 7; the centres of these spheres lie in

four different planes parallel to the plane of projection, and are therefore distinguished by circles drawn in heavy or light, continuous or broken lines. The adjustment of the positions of the tetrahedral groups which accompanies the shifting of the carbon spheres, and indeed the entire process, is compatible with the maintenance of cubic symmetry; the existence of the coincidence movements of the system involves that all the cavities for the reception of the tetrahedral groups remain identical with one another.

One of the surest indications of close packing is obtained when each sphere is in contact with, or in very close proximity to, such a number of surrounding spheres as approaches the maximum. The number of contacts and near proximities in the assemblage under consideration is as follows: for each of the carbon spheres, 19, namely, 6 with carbon spheres and 13 with hydrogen spheres. For each of three-fourths of the hydrogen spheres, 8, namely, 4 with carbon spheres and 4 with hydrogen spheres; for each of one-fourth of the hydrogen spheres, 7, namely, 4 with carbon spheres and 3 with hydrogen spheres. These numbers of contacts approach the maxima, taking into account the different sizes of the component spheres; they thus afford a proof that the marshalling of the assemblage is compatible with very close packing.

In connexion with the partitioning of the assemblage into identical molecular units of the composition CH_4 , it should be noted that four of the thirteen contacts of hydrogen spheres with a carbon sphere are nearly symmetrically distributed over the surface of the latter; the four hydrogen spheres concerned are thus situated at the apices of an approximately regular tetrahedron, of which the centre is the centre of the carbon sphere. The four hydrogen spheres referred to may be identified as follows. In any pseudo-cubic group of eight carbon spheres in the assemblage, the single trigonal axis intersects two of the eight; one of these makes contact with a single hydrogen sphere of the enclosed group at its point of intersection with the trigonal axis. Regarding this carbon sphere as that of the molecular unit, CH_4 , to be picked out, it is to be noted that the three contacts with it of hydrogen spheres, which, with the one on the trigonal axis, make up the four referred to, are those of the hydrogen spheres lying in three of the outside hollows of those faces of the cubic group which have as their common angular point the centre of the selected carbon sphere. The four contacts of the unit molecular group CH_4 thus derived do not precisely mark the angular points of a regular tetrahedron, but the arrangement of the four hydrogen spheres about the carbon sphere approximates so closely to the regular tetrahedral disposition

premised by the theory of van't Hoff and Le Bel (Figs. 8 and 9) that its departure from the latter cannot be clearly indicated in a diagram; the assemblage is divisible into identical units of the form depicted. The result of the close approximation to regularity of the tetrahedra marked out by the hydrogen sphere centres thus selected is that different assemblages produced by fitting together the molecular units in different orientations will be so nearly identical that the equilibrium arrangements to which they pass will be actually identical. In this connexion it is instructive to observe that the tetrahedral arrangement is indicated in another manner; each carbon sphere, before the adjustment, is similarly related to eight cavities, of which the relative positions are those of the angular points of a cube, and the greatest number of these cavities which can participate in containing the hydrogen spheres attached to the carbon sphere is four. Consequently, the most symmetrical mode

FIG. 8.

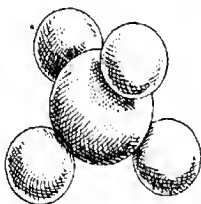
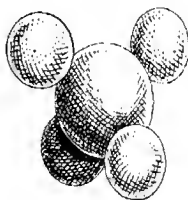


FIG. 9.



of allotment of the hydrogen spheres is for each carbon sphere to attach to itself four hydrogen spheres contained in four out of the eight cavities surrounding it, and for these four cavities to be selected with a regular tetrahedral disposition. Thus, like the hydrogen atoms in the usual graphic formula of methane, the four cavities concerned have interchangeable positions with respect to the carbon sphere to which they relate.

It is thus to be finally concluded that the investigation of the close-packed arrangement of the methane assemblage indicates that the molecular units can be so chosen as to have the tetrahedral configuration depicted in Figs. 8 and 9.

The relation thus established between the theory of the tetrahedral arrangement of the links within the molecule, based on the chemical behaviour of methane and its derivatives, and the concrete geometrical properties of the corresponding close-packed arrangement of the spheres of influence of the component atoms is of fundamental importance. It is worth recapitulating in precise language because it will subsequently be shown that a relation of the same

nature obtains for the carbon compounds generally; in other words, that a tetrahedral arrangement of the contacts of a carbon sphere of influence with its companion spheres persists after substitution has taken place. The relation for methane may be thus stated. Represent the carbon and hydrogen atoms of a methane molecule by spheres of the valency volumes 4 and 1 respectively, and form the spheres into groups of five according to the van't Hoff-De Bel theory, each sphere of volume 4 being in contact with four spheres, each of volume 1, placed around it symmetrically, so that their centres mark the angular points of a regular tetrahedron; it is then found that, while preserving the marshalling of the spheres of each individual molecular unit, a close-packed assemblage can be formed by fitting the groups together symmetrically, of such a nature that its geometrical properties are those of the crystalline tetrahalogen derivatives of methane.

The following crystallographic data are available as bearing on the symmetry and dimensions of the methane assemblage. Carbon tetraiodide, CI_4 , is cubic, and carbon tetrabromide, CBr_4 , crystallises above 46.7° in the cubic system, the crystal class being known in neither case. Below 46.7° , carbon tetrabromide crystallises in the monosymmetric system, but, as previously pointed out (Trans., 1908, 93, 1530), this modification is referable to the pseudocubic axial system, $a:b:c=1.0260:1:1$, $\alpha=90^\circ 16'$, $\beta=\gamma=90^\circ 33'$; the monosymmetric form thus scarcely differs in dimensions from the truly cubic one, and both indicate the cubic marshalling of the assemblage. On replacing each hydrogen sphere in the methane assemblage by the group CH_2Br , in accordance with the second geometrical property of close-packed assemblages (Trans., 1907, 91, 1204), tetrabromo- $\beta\beta$ -dimethylpropane, $\text{C}(\text{CH}_2\text{Br})_4$, is obtained; as Jaeger has found (Trans., 1908, 93, 520), this substance may be regarded as pseudocubic, with the axial ratios $a:b:c=1.0484:1:0.9472$, $\beta=90^\circ 45'$. The cubic marshalling of the methane or carbon tetrabromide assemblage thus survives the symmetrical introduction of four methylene groups, CH_2 , into each molecular unit, CBr_4 , in accordance with the second geometrical property.

In connexion with the assemblage attributed above to methane and to its fully substituted halogen derivatives, it may be noted that iodoforn, CHI_3 , is described as hexagonal with $a:c=1:1.1084$ (Pope, Trans., 1899, 75, 46). It is evident that the symmetry of the space arrangement of the methane assemblage may be lowered without any appreciable alteration of the relative situations of the spheres by a partial substitution of the spheres representing hydrogen atoms which leads to the production of an arrangement

appropriate for iodoform. In order to trace the probable effect of such a substitution, it is convenient to work with an ideal less closely packed assemblage of higher symmetry, from which the methane assemblage may be regarded as derived. Let the centres of the carbon spheres occupy precisely the points of a cubic space-lattice (Fig. 3), and let each of the tetrahedral groups, CH_4 , which are now to be of completely regular configuration, be rotated from the orientations which they present in the closest-packed assemblage, so that the centres of the small spheres all lie on trigonal axes; the system thus consists of units of the composition CH_4 , less closely packed, but all similarly orientated. Next substitute iodine spheres for three of the four hydrogen spheres of each unit, without altering the positions of the centres, in such a way that the new units, CHI_3 , are all similarly orientated; the result is to destroy three-fourth of the trigonal axes, and to leave only those which contain the centres of the unsubstituted hydrogen spheres. On performing finally the rotations and adjustments requisite to restore the closest-packed condition prevailing in the methane assemblage, three-fourths of the surviving trigonal axes are destroyed. The closest-packed assemblage thus arrived at has rhombohedral symmetry and is pseudocubic.

In the assemblage just derived let the dimension c be three times the distance between the centres of carbon spheres lying on the same trigonal axis; the distance separating these centres along directions perpendicular both to this axis and to a face diagonal of a cube of the pseudocubic partitioning will be approximately $\sqrt{2}c/3$. If the latter distance is taken as $a/2$, the axial ratio is obtained as:

$$a:c = 2\sqrt{2}:3 = 1:3/2\sqrt{2} = 1:1.0606.$$

This ratio is not far removed from that of iodoform, and it is therefore established that the rhombohedral form displayed by the crystalline substance may, like the rhombohedral assemblage suggested, be pseudocubic.

The Normal Homologues of Methane.

The most obvious method of constructing assemblages representing hydrocarbons homologous with methane consists in symmetrically removing one or more hydrogen spheres from the groups of four contained in the assemblage of the parent hydrocarbon, and then, by appropriate adjustment of the spheres remaining, to close up the gaps which have been produced.

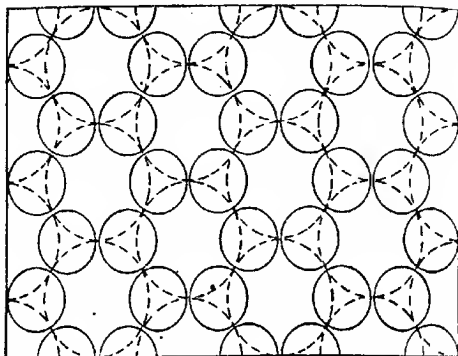
Thus, an assemblage of the empirical composition CH_3 may be derived by symmetrically removing a hydrogen sphere from each group of four in the methane assemblage, and then adjusting so that with the same number of cavities each cavity among the carbon

spheres shall be as closely packed as possible, although now containing but three hydrogen spheres instead of four. Such an operation corresponds with the removal of the iodine atom from methyl iodide; the observed fact that in this reaction, as in all similar ones, the condensation of two hydrocarbon radicles yields one molecule, finds expression in the way in which the assemblage undergoes contraction during the adjustment necessary for closing up the produced gaps. The fact that the methyl iodide assemblage, which has the same marshalling as that of methane, yields ethane on treatment with sodium, can be represented as follows. In the methane assemblage, the carbon spheres are prevented from making intimate contact with one another by the presence of hydrogen spheres packed around them, but when the number of the latter is reduced by each group of four becoming a group of three, the carbon spheres necessarily draw nearer together; it is conceivable that equilibrium, represented by close-packing, requires them to come into closer contact, and to press on each other two by two, and that the intimate relationship thus established between the individuals of a pair corresponds with the linking between the two methyl carbon atoms in the ethane molecule. It will be shown in connexion with the assemblage described below that the condensation of the assemblage following elimination of hydrogen spheres and the adjustment which restores close-packing, lead to close contact of the kind referred to between carbon spheres; such contact is thus representative of the formation of a link between carbon atoms such as that present in the ethane molecule.

The production of the ethane assemblage from that of methane may also be regarded as resulting from the replacement of one-fourth of the hydrogen spheres, each by one carbon sphere, when, in accordance with the second geometrical property of close-packed assemblages, the introduction of three hydrogen spheres with each new carbon sphere suffices for the preservation of close-packing. The alternative ways in which the paraffins may be regarded, such, for instance, as the possibility of considering propane as dimethylmethane and as ethylmethane, also find expression in the geometrical mode of regarding these substances now advanced. The most general method of formulating the normal paraffins consists in assigning to them the constitution $\text{H} \cdot (\text{CH}_2)_n \cdot \text{H}$, in which an open chain of n -carbon atoms forms the backbone of the molecule, and is isolated from other similar chains in front and rear by the addition of a hydrogen atom to each of the end methylene groups. For the present purpose it will therefore be convenient to derive first an assemblage of the empirical composition CH_2 , corresponding with the radicle methylene; it will then be shown how this assem-

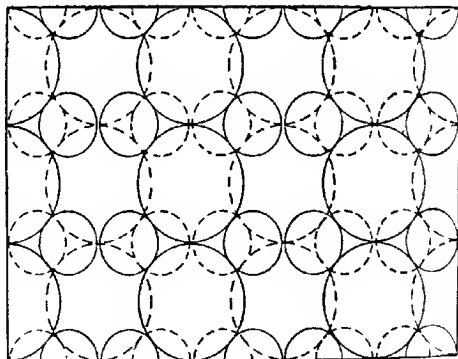
blage, composed of strings of methylene groups the carbon spheres of which are in close contact throughout the length of the string, is related to that of methane, and in what manner hydrogen spheres

FIG. 10.



can be homogeneously intercalated so as to divide the methylene strings of indefinite length into definite molecular groups to represent any individual normal paraffin.

FIG. 11.



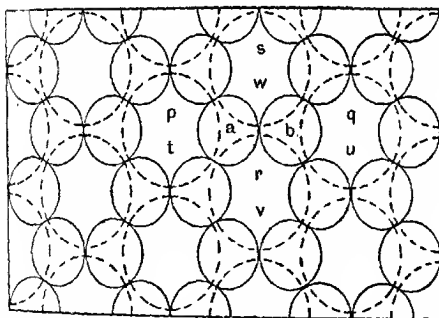
The general methylene assemblage may be constructed in the following manner. Space is divided into endless hexagonal prisms, each of which is divided into identical hexagonal cells by describing

a series of parallel planes perpendicular to the prism axes at a distance apart equal to the smaller diameter of the prisms. In each prismatic cell thus obtained is inscribed a sphere; the diameter of the latter will be the smaller diameter, and also the height, of the hexagonal cell. In the system produced, each cell corner marks the centre of a cavity between adjoining spheres, and about each meeting point of cell corners a small sphere is now described of such diameter as just to touch the six surrounding large spheres. The resulting system is shown in plan in Fig. 10, and in elevation in Fig. 11, and possesses a general arrangement which may be visualised by the perspective view of a fragment shown in Fig. 12. Each small sphere of the assemblage, in addition to making contact with six large spheres, is nearly in contact with three other small spheres, and each large sphere is in contact with twelve small spheres and eight large ones. If the large spheres represent carbon, and the smaller ones hydrogen atoms, the assemblage has the empirical composition CH_2 ; since, however, the volume of the smaller spheres is appreciably less than one-fourth that of the larger, the valency

FIG. 12



FIG. 13.

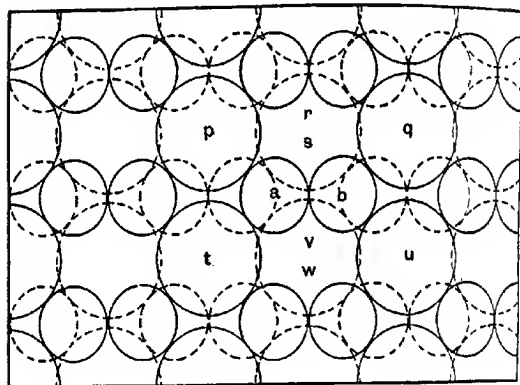


elation of the volumes requires the smaller to increase until the volumes of small and large spheres, with the addition of the appropriate proportions of interstitial space, are in the ratio of 1 : 4. This expansion of the small spheres necessarily forces the larger spheres apart, and for this to occur in such a manner that the modified system possesses maximum closeness of packing, it must take place so as to break as few of the contacts as possible in a

symmetrical manner. The most symmetrical expansion of the kind which can occur is one which breaks all the contacts between large spheres and converts the assemblage of Figs. 10 and 11 into that represented in Figs. 13 and 14; the smaller number of contacts in the modified system is indicative of looseness of packing, and in order to reproduce close-packing as many of the original contacts as possible must be re-established in a symmetrical manner.

A consideration of the assemblage of Figs. 13 and 14 in connexion with the cubic disposition of large spheres shown in Fig. 4, from which the methane assemblage was derived, shows that the plane arrangement of the large spheres in their layers, shown by the continuous line circles of Fig. 14, is approximately that obtaining in the layers of the assemblage of Fig. 4, which are parallel to

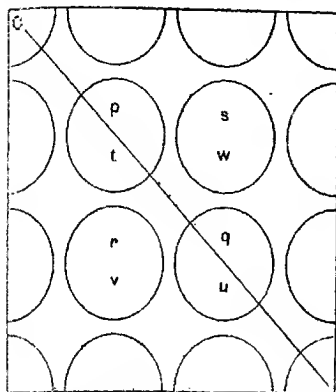
FIG. 14.



the plane the trace of which is the diagonal line C in Fig. 13, as shown by the continuous line circles of Fig. 16. Whilst, however, in Figs. 15 and 16 each cavity between the large spheres is destined and is sufficient for the accommodation of a tetrahedral group of four small spheres, the corresponding space in Figs. 13 and 14 has been reduced so that it can accommodate but two small spheres; this has been effected by somewhat increasing the distance between the large sphere centres in the direction of the diagonal C in Fig. 15, and considerably diminishing the distance between the layers of sphere centres in the direction perpendicular thereto. Each cavity which suffices to contain four small spheres, such as i enclosed by the eight spheres, four, p, q, r, and s, of one plane of Fig. 15, and four, t, u, v, and w, of the plane immediately below, is

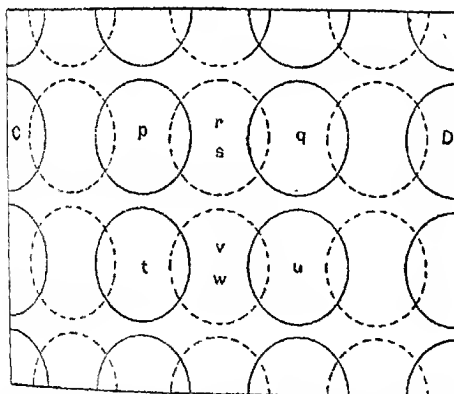
shown in Figs. 15 and 16, has by the process just described been converted into two cavities, namely, one enclosed by the correspond-

FIG. 15.



ing spheres, p, r, s, t, v, and w, of Figs. 13 and 14, the other by the spheres, q, r, s, u, v, and w. The two small cavities thus derived

FIG. 16.

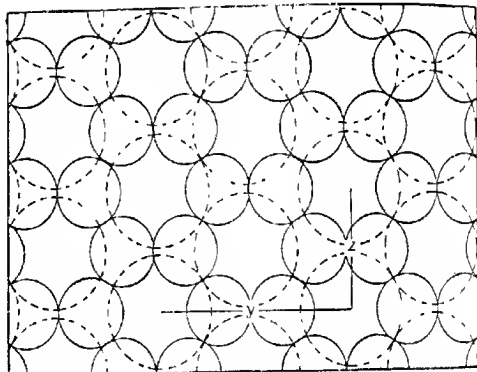


from the original large one each suffices for the accommodation of one small sphere; these are marked a and b in Figs. 13 and 14.

The process by which the present assemblage can be derived from that of methane, and also the converse, by which the former can be converted into the latter, are applications of the second geometrical property of close-packed homogeneous assemblages.

It remains to indicate the manner in which close-packing can be established in the assemblage of Figs. 13 and 14, that is to say, the way in which the assemblage can be caused to occupy the minimum space as the result of an adjustment which does not involve re-marshalling. The requisite deformation will be understood by considering its effects on the system; these are indicated in Fig. 17, which represents one double layer of the two kinds of spheres, and in Figs. 18 and 19, which are projections of the altered assemblage

FIG. 17.



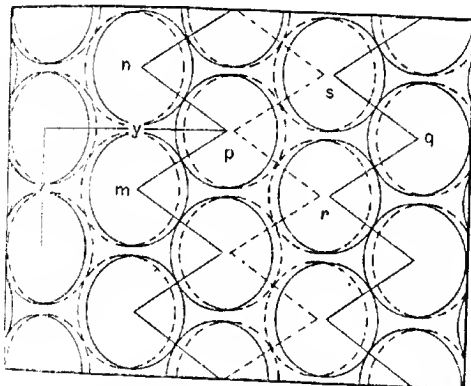
on two planes at right angles to one another. For the sake of clearness, the hydrogen spheres are omitted from Fig. 18.

The symmetrical adjustment which increases the closeness of the packing brings the members of the rows of carbon spheres shown in Fig. 13 alternately into contact and further apart, as indicated in Figs. 17 and 18; thus a carbon sphere, such as *p*, makes contact only with *m* and *n*, and draws away from *r* and *s*. The sequence of making contact and moving further apart alternates in consecutive layers of the form shown in Fig. 17, so that these layers now have two distinct projections on the same area of Fig. 18; the latter diagram thus shows two alternating sets of carbon spheres, those indicated in continuous lines, and those in dotted circles, in place of the one set shown in Fig. 13. This alternation results in the formation, in each of the planes projected on Fig. 18, of zigzag

strings of carbon spheres in contact and of indefinite length, the zigzag strings in one plane of the assemblage being located from the positions of others in the same plane or of those in the next neighbouring planes by some simple symmetrical operation such as that about a centre of symmetry; the zigzag strings in one plane do not lie immediately beneath or above those in the next plane.

The assemblage of Figs. 17, 18, and 19 represents the general methylene assemblage, and is to be regarded as an arrangement having the empirical composition CH_2 , which constitutes the open-chain portion of a normal paraffin. By dividing the zigzag strings into fragments of suitable length by the introduction of pairs of hydrogen spheres at appropriate intervals, it may be converted, as is shown below, into an assemblage of molecular aggregates repre-

FIG. 18.

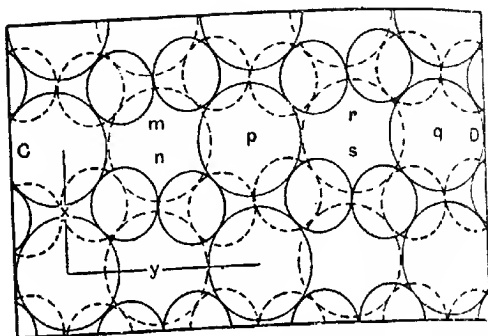


sentative of any particular normal paraffin. The existence of this correspondence between the feature of close-packed assemblages just described and the observed fact that, in the normal paraffins, the chains of methylene radicles connecting the terminal methyl groups exhibit behaviour which warrants the representation of the normal paraffins by the general formula $\text{CH}_3 \cdot [\text{CH}_2]_n \cdot \text{CH}_3$, is worthy of note.

It has been shown in previous papers that the configurations assignable, in accordance with the crystallographic evidence and with the theory of homogeneous close-packing, to numerous organic substances is in entire accord with some features of the chemical behaviour of such compounds. Before proceeding to employ the configuration arrived at for the general methylene chain, $[\text{CH}_2]_n$, in the production of assemblages representing the normal paraffins

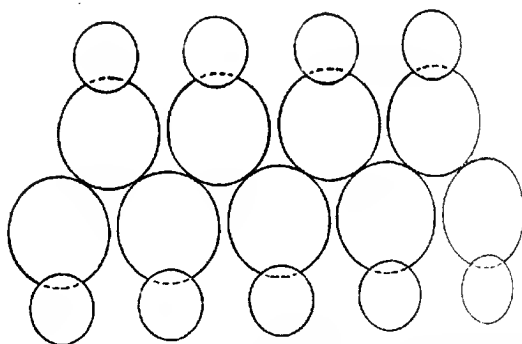
for comparison with the chemical facts and crystallographic evidence, it is therefore desirable to consider stereochemical features of the chain, $[\text{CH}_2]_n$, as now presented. Any such continuous chain separated from the whole assemblage presents the plan and elevation

FIG. 19.



shown in Figs. 20 and 21; a rough perspective view of a fragment of the indefinitely prolonged chain is given in Fig. 22. It will be seen that each carbon sphere is directly attached to two other carbon

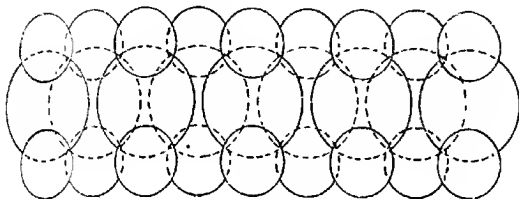
FIG. 20.



spheres and to two hydrogen spheres, and that the plane containing the centres of the three carbon spheres is perpendicular to the plane drawn through the centres of the two hydrogen spheres and that of the carbon sphere which they touch. Further, it will be

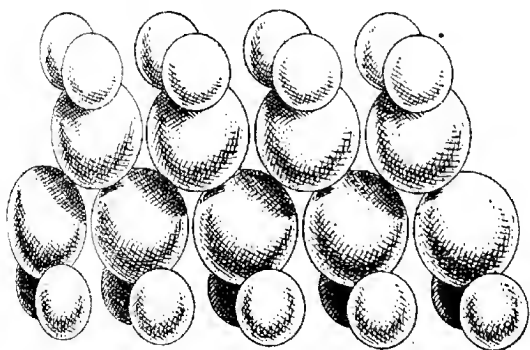
seen that by joining the four points of contact made on each carbon sphere, two by hydrogen and two by carbon spheres, a tetrahedron results. Since these are the essential features of the environment of any carbon atom of the chain in a normal paraffin, as summarised by the theory of van't Hoff and Le Bel, it follows that the con-

FIG. 21.



figuration for the chain deduced above is in accordance with the chemical facts. In this connexion, it is interesting to recall the interpretation usually put on the important fact of the persistence of the tetrahedral arrangement of links from term to term of the series of assemblages representing the normal paraffins. Adopting

FIG. 22.



the method employed by van't Hoff and Le Bel, the configuration of a string of methylene complexes which forms the backbone of a normal paraffin molecule is derived by first substituting carbon atoms for two of the tetrahedrally disposed hydrogen atoms of a methane molecule, preserving the tetrahedral disposition of the links, and then attaching two hydrogen atoms to each added carbon

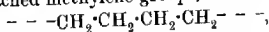
atom in such a way that the two outer methylene complexes thus formed are identical with the central one and identically related to it, while having the opposite orientation. The central portion, $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot$, of the propane molecule is thus arrived at. Arrangements proper for the representation of succeeding terms of the homologous series of paraffins are derived by repetitions of the same process.

The form of a group of methylene complexes reached in this way is quite definite and is that shown in Fig. 22; as the preceding argument has established, a number of the groups representing the same term of the series can be packed closely together so that the passage to closest-packed equilibrium involves but a quite trivial adjustment. When additional hydrogen spheres are inserted appropriately to complete the representation of a given paraffin, an assemblage results, as will be shown immediately, which displays the geometrical and dimensional properties appropriate to the crystal of the substance concerned.

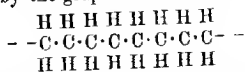
It is easy to demonstrate that the persistence of the tetrahedral type of arrangement is a geometrical consequence of substitution effected in accordance with the second geometrical property. For in carrying out such a substitution in a methane assemblage, the added carbon spheres are deposited in the hollows on the faces of the layers of the assemblage left vacant by the removal of hydrogen spheres, and consequently the incoming large spheres occupy practically the same situations with respect to the unsubstituted portions of the assemblage as were previously occupied by outgoing small spheres. Consequently, since the situations of the paraffin spheres give a tetrahedral arrangement of the contacts within a molecular group, this tetrahedral disposition of the contacts still obtains after the substitution. It is not suggested that the tetrahedral arrangement of the contacts will remain precisely regular.

The Ethane Assemblage.

The unit, shown in Fig. 22, of the general methylene assemblage of Figs. 17, 18, and 19 possesses the constitution of an indefinitely long string of attached methylene groups,

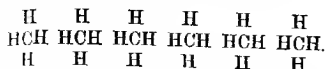


and is represented by the graphic formula:

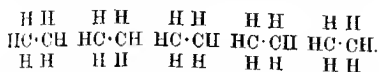


The comparison which has been made between the general methylene assemblage and the methane assemblage shows that if extra pairs of hydrogen spheres are introduced between succeeding

carbon spheres, the resulting assemblage assumes the composition and constitution of methane, thus:



If, however, such pairs of hydrogen spheres are intercalated, not everywhere between succeeding carbon spheres, but intermittently at points homogeneously selected, the resulting assemblage should represent a normal paraffin homologous with methane. On introducing pairs of hydrogen spheres symmetrically at half the points indicated, the assemblage representing ethane should be produced, thus:



It is desirable to confirm this deduction by an examination of the ethane assemblage, thus derived, in the light of the principal crystallographic evidence available; this is found in the data obtained by Gossner for the hexahalogen derivatives of ethane and for pentabromoethane (Trans., 1906, 89, 1682). In the tabulated data for these substances it is convenient to double the ratio of c to b , and to state the equivalence parameters and axial ratios as in the appended table; the valency volume, $V=14$, is regarded as the molecular space unit, so that the linear unit employed for the equivalence parameters is the edge of a cube of unit valency volume. The closeness of the packing of the spheres is taken to be the same as that of the closest-packed assemblage of equal spheres:

| | $a : b : c$ | β | $x : y : z$ |
|---|---------------------|---------|--------------------------|
| $\text{C}_2\text{H}_2\text{Cl}_4$ | 0.5677 : 1 : 0.6320 | 90° | 1.9255 : 3.3917 : 2.1435 |
| $\text{C}_2\text{H}_2\text{Br}_4$ | 0.5612 : 1 : 0.6342 | " | 1.9086 : 3.4009 : 2.1520 |
| $\text{C}_2\text{H}_2\text{Cl}_2\text{CBrCl}_2$ | 0.5646 : 1 : 0.6384 | " | 1.9120 : 3.3867 : 2.1620 |
| $\text{C}_2\text{H}_2\text{CBr}_2$ | 0.5639 : 1 : 0.6284 | " | 1.9205 : 3.4058 : 2.1403 |
| $\text{C}_2\text{HBr}_2\text{CBr}_2$ | 0.5650 : 1 : 0.6236 | 91°19' | 1.9262 : 3.4126 : 2.1281 |
| Mean for first four substances : | | | 1.9166 : 3.3963 : 2.1494 |

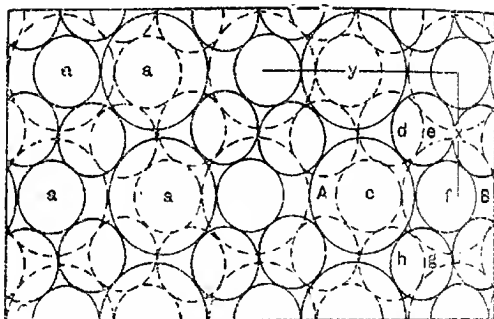
In calculating the mean equivalence parameters, the four orthorhombic substances only have been considered, the monosymmetric pentabromoethane being excluded from the calculation.

It has now to be considered how the general methylene assemblage of Figs. 17, 18, and 19 can be converted into a close-packed assemblage of the dimensions represented by the above mean equivalence parameters, $x : y : z = 1.917 : 3.396 : 2.149$, by the intercalation of pairs of hydrogen spheres in the manner already indicated. The diameter of a univalent sphere is obtained in terms of the linear unit from the consideration that it is the face-diagonal of the cube outlined by joining the obtuse solid angles of the unit dodecahedron

of a closest-packed assemblage of these spheres (Trans., 1907, 91, 1181). Thus, if a be the diameter in question, $a/\sqrt{2}$ is the edge of the cube inscribed in the unit dodecahedron; the content of this cube is $a^3/2\sqrt{2}$, and that of the dodecahedron is equal to $a^3\sqrt{2}$, which is taken as unity. Consequently, $a=2^{\frac{1}{3}}=1.1225$, and since the volume of a quadrivalent sphere is four times that of a univalent one, the diameter of the former is $2^{\frac{3}{4}} \times 2^{\frac{1}{4}} = 2^{\frac{1}{2}} = 1.7818$.

The sphere projections in the general methylene assemblage of Figs. 17, 18, and 19 are drawn to the scale thus indicated, and the dimensions indicated in these figures are, two of them, the values, $x=1.917$ and $y=3.396$, of the mean equivalence parameters in the table last given. On introducing between each pair of layers of the general methylene assemblage extra hydrogen spheres equal in number to the carbon spheres already present, the preservation of

Fig. 23a.



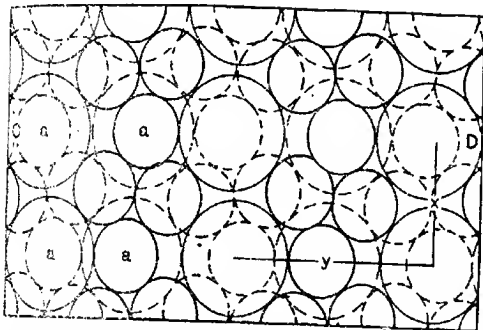
close-packing demands that the one pair shall shift upon the next pair, so that the projection of the two pairs now consists of four superposed sections, as depicted in Figs. 23, *a* and *b*.

In these diagrams, which, taken together, give a projection of the ethane assemblage, some of the intercalated hydrogen spheres are marked *a*; the dimensions, $x=1.917$ and $y=3.396$, are shown in the plane of the section. The packing is about as close as in the methane assemblage described above, and since the closeness of the packing is thus adhered to and the composition is that corresponding with ethane, the translation perpendicular to the plane of the section will necessarily have the corresponding value of $z=2.149$. Since the valency volume of the molecular unit is 14, and that of the terminal hydrogen spheres is 2, the dimension z of the methylene assemblage, as shown in Figs. 17 and 18, is six-sevenths of the z value

just stated, and therefore equals 1.842; this is the value of z used in these diagrams. It is concluded from the above that the assemblage depicted in Fig. 23 is related to the general methylene assemblage in the appropriate manner, and has the dimensions indicated for ethane by the crystallographic data; the crystalline symmetry of the assemblage, when all the smaller spheres are identical in kind, is the orthorhombic symmetry exhibited by the hexa-halogen derivatives of ethane named in the table. It is, however, obvious that differences in kind occurring among the smaller spheres might have the effect of reducing the symmetry of the assemblage in the manner indicated by the existence of the monosymmetric penta-bromoethane.

Lehmann has shown (*Molekular-Physik.*, 1888, 1, 178) that hexa-

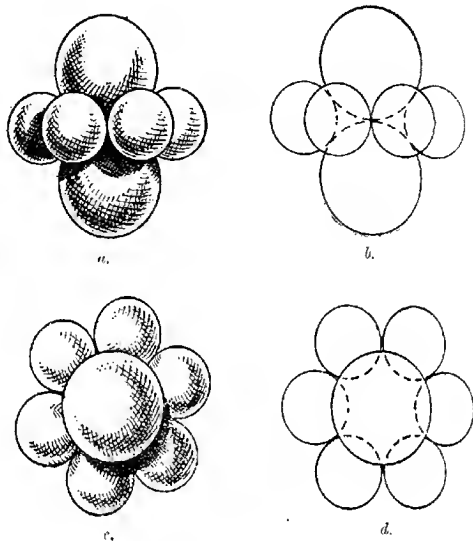
FIG. 23b.



chloroethane, C_2Cl_6 , crystallises in an anorthic and a cubic form as well as in the orthorhombic form dealt with above; no measurements are available for the former modification, but it is instructive to deduce the assemblage representing the cubic form of the substance. In view of the close relationship which must exist between the orthorhombic and the cubic modifications of hexachloroethane, it is convenient to derive the assemblage for the latter from that of the former. The orthorhombic assemblage may, for purely crystallographic purposes only, be regarded as built up from a unit of the form shown in Fig. 24, a , b , c , and d , and consisting of two carbon spheres in contact having a circlet of six chlorine spheres placed round the neck produced between the two large spheres; the volumes of the two kinds of spheres, namely, 4:1, are such that when all the six small spheres touch the two larger ones, they very approximately form a continuous ring of small spheres in

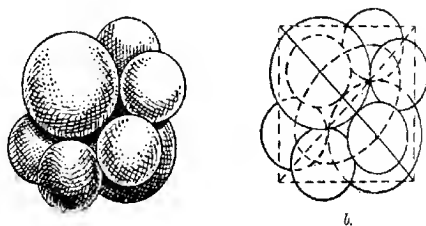
contact as shown in the diagrams. A geometrical unit of this kind is marked ABCdefgh in Fig. 23*a*, and presents in that diagram the

FIG. 24.



aspect depicted in Figs. 25 *a* and *b*; it can be used in the manner described below for the construction of the assemblage representing the cubic modification of hexachloroethane.

FIG. 25.



The geometrical units referred to and figured occupy the valency volume, $W=14$, and can be fitted together in cubic symmetry so

that their centre points lie at the centres of the cube cells of a cube partitioning of space provided that the cube cells have the volume 11; the length of the cell edge should therefore be $\sqrt[3]{14}$, the scale previously used being adopted. The units are fitted into a system of non-intersecting trigonal axes of the kind already described (p. 2317), and in the following manner. In one cube cell the trigonal axis of which has the direction indicated by *a* (Fig. 54), place a geometrical unit group so that its centre is at the centre of the cube cell, and so that the centres of its two large spheres lie on the single trigonal axis of the cell; whatever the position of the small spheres, it is evident that their centres lie on a circle the centre of which is the point of contact of the two large spheres, and the plane of which is perpendicular to the trigonal axis of the unit. This circle is projected on one of the three face directions of the cube cells as an ellipse, as indicated in Fig. 25*b*. Geometrical units are now fitted in similar manner into the other cube cells of the system, due regard being paid to the preservation of the respective trigonal axes, *a*, *b*, *c*, and *d*, of the different cells at the partitioning.

A single layer of the resulting system of cells with their contents is depicted in Fig. 26 as a projection on a cube plane; the projections of the trigonal axes are shown as continuous straight lines, and are lettered *a*, *b*, *c*, and *d*, in accordance with the convention previously adopted (Trans., 1907, **91**, 1183). Digonal axes of rotation pass through the assemblage perpendicular to the plane of projection at the points S, T, U, and V.

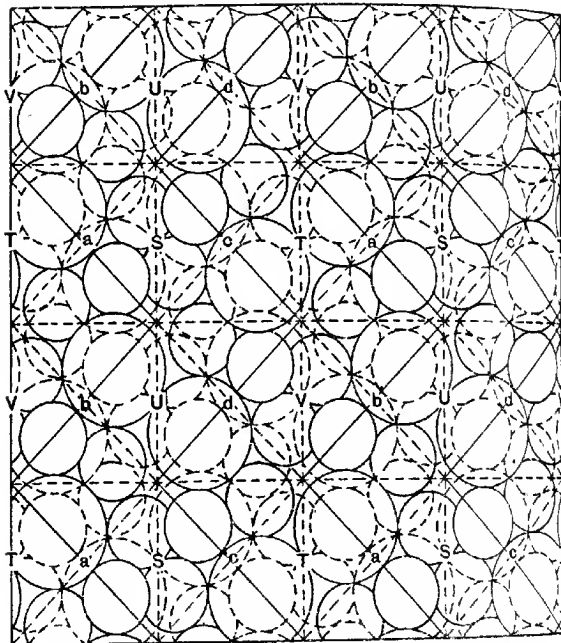
The precise position of the small spheres in the assemblage is deduced by reference to the digonal axes of symmetry. Thus the geometrical unit is so placed in the cube cell of the partitioning that the distance of the centre of one of its small spheres from a digonal axis is equal to the radius of the small sphere; this condition is practically fulfilled if the position of the circlet of small spheres is such that the centre of one of them lies at the highest point of the circular locus, the projection of this centre therefore falling at one extremity of the minor axis of the ellipse in which the circular locus is projected on the plane of a cube face. When one geometrical unit has been placed in position in the manner indicated, others can be similarly located with their centres at the remaining cell centres by carrying out the coincidence movements and operations with respect to the axes of the first selected cell. The type of symmetry is that numbered $2a_1$ in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, **23**, 44).

It is evident from Fig. 26 that the spheres of the single layer of complexes fit closely together in the marshalling indicated, and,

as the assemblage can be regarded as made up of such layers parallel to either of the three directions of the cube faces, it follows that the geometrical units employed can be fitted together in space in the manner indicated, and that the packing is very close.

The geometrical unit which has been used in building up the orthorhombic and the cubic crystalline assemblage of hexachloroethane is, as before mentioned, merely used for constructional

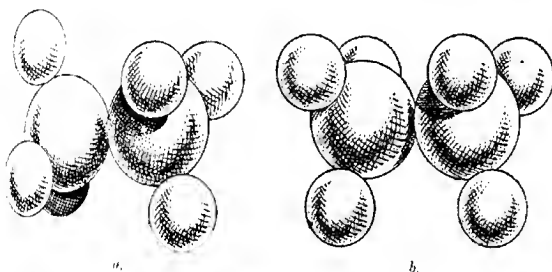
FIG. 26.



purposes, and is not to be regarded as possessing the configuration of the chemical unit or molecule. The possession of a larger mass of crystallographic data than is at present available should enable the configuration of the chemical molecule to be determined by a process of elimination. The various polymorphous forms of the different halogen derivatives of ethane must all consist of packed arrangements of units having the configuration of the ethane molecule; further, the latter must be derivable from the general

methylene assemblage by the symmetrical intercalation of spheres of unit valency volume in this assemblage, as already described. These conditions are fulfilled, not only by the geometrical unit used above, but also by groups of the composition C_2Cl_6 possessing a configuration such that the eight component spheres are centred at the apices of two tetrahedra so placed that an apex of the one is directed towards an apex of the other. The two kinds of unit of the structure thus distinguished possess the configuration of the ethane molecule as it has been deduced from the principles laid down by van't Hoff and Le Bel; rough perspective views of the chemical unit or molecule thus derived are given in Figs. 27 *a* and *b*.

FIG. 27.



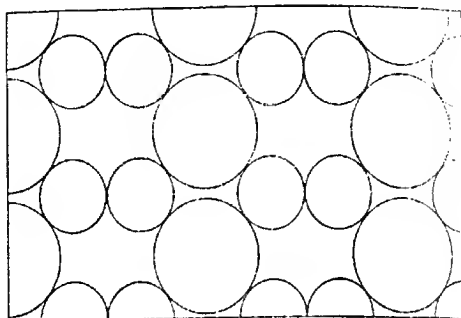
It will be seen that the one may be derived from the other by rotating one-half of the unit through 180° with respect to the other half. The fact that these two configurations of unit, closely related by the mode in which one is convertible into the other, can be traced in the assemblage as depicted in Fig. 26, is of interest in connexion with van't Hoff's doctrine of the free rotation of a singly bound carbon atom.

An Alternative General Methylene Assemblage.

A simple method has been given above (p. 2333) for deriving an assemblage which can be geometrically partitioned into endless strings of the general form $n(CH_2)$, and it has been shown how the assemblages representative of the normal paraffins can be derived from this general methylene assemblage by the intercalation of hydrogen spheres. Examination shows, however, that by modifying the assemblage referred to by means of a particular kind of distortion, an alternative series of assemblages is obtained, in which the arrangement of the carbon and hydrogen spheres which form the methylene fragments is very nearly the same as before: this

arrangement, like the first, is related to a number of crystallographic facts. The new kind of arrangement can be derived from the first by an adjustment or deformation which leaves each sphere with

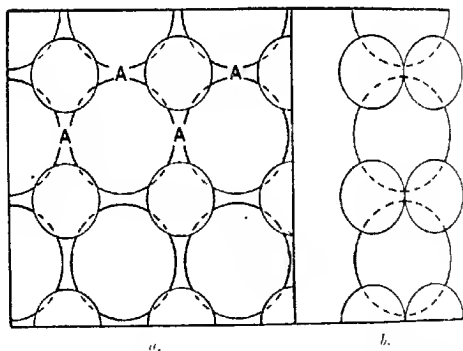
FIG. 28.



practically the same surroundings but which changes the general symmetry: the nature of the adjustment is as follows.

The large spheres of one layer (Fig. 28) in the unadjusted methylene assemblage of Fig. 14, when pressed together in the direction which

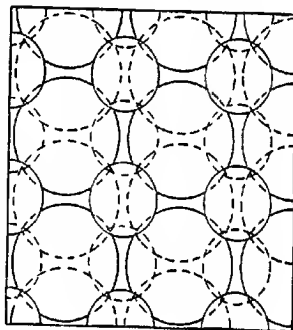
FIG. 29.



is horizontal in the diagram, fall into a square arrangement. simultaneously, the smaller spheres, by movement on each other and on the large spheres with which they are in contact, are able to accommodate themselves to the altered form of the layer, and

can pack very closely into the hollows remaining after the change is made. The section of the assemblage shown in Fig. 28 thus becomes that shown in Fig. 29 *a* and *b*; the modified layer consists of a plane of the larger spheres in square arrangement with the smaller spheres sunk in the hollows on both of its faces; the small spheres touch each other in the plane drawn through the centres of the large spheres, as shown in Fig. 29*b*. Layers produced in this manner can be fitted closely together in such a way that the resulting assemblage is practically identical with that previously reached by compounding the layers in their other shape. In other words, the layers depicted in Fig. 29 are obtained from the general methylene assemblage of Fig. 14 if, instead of making the separation into layers parallel to the plane of Fig. 14, it is made parallel to the plane of projection of the same assemblage shown in Fig. 30. The plane of projection of Fig. 30 is at right angles to those of both Figs. 13 and 14; thus, in Fig. 31*a*, in which the arrangement is identical with that in Fig. 13, a plane perpendicular to the plane of the diagram, drawn through AB, gives the projection shown in Fig. 14, whilst a plane drawn through CD, also perpendicular to the plane of Fig. 31*a*, gives the section depicted in Fig. 31*b*.

FIG. 30.



The conversion of the general methylene assemblage depicted in Fig. 30 into that representing a normal paraffin is, as before, effected by intercalating hydrogen spheres, twice as numerous as the carbon spheres in a single layer, between consecutive layers of carbon spheres appropriately selected, the planes of these layers being parallel to the plane of projection of Fig. 30. It is seen from Fig. 29*a* that the principal hollows, which are of the kind marked A, in one of the surfaces of a layer are twice as numerous as are the carbon spheres of the layer; if therefore two such layers are appropriately placed together, a layer of hydrogen spheres twice as numerous as the carbon spheres of a layer can be closely fitted between them, each sphere occupying a principal hollow, such as A, on both the opposing faces. The combination of two layers of the composition CH_2 with the layer of hydrogen spheres thus fitted between them, is shown projected in Fig. 32: the small spheres

of the intercalated layer are indicated by double circles. In the assemblage representing a normal paraffin formed in this manner the

FIG. 31a.

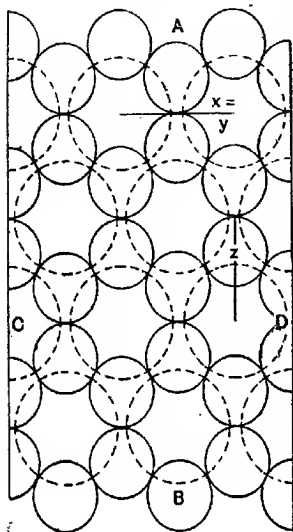
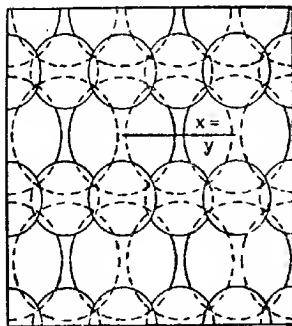
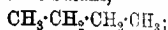


FIG. 31b.



hydrogen spheres added to a terminal layer of the form CH_2 , and allotted to this layer, occupy the same positions in the face of the layer as they would if an additional CH_2 layer, of which they formed part, were added; this can be seen on inspection of the projection of a stratum of a paraffin assemblage of the form under consideration. The stratum represented in Figs. 31 a and b is that appropriate to normal butane,



corresponding with the four methylene radicles, CH_2 , there are present four layers of large spheres in each stratum, as shown in Fig. 31a.

The centres of the terminal small spheres which have been introduced lie on two similar sets of digonal axes of the assemblage having two directions perpendicular to one another as indicated by the diagonal broken lines of Fig. 32; the identity of these digonal axes in the two directions involves the presence of screw tetragonal axes perpendicular to the planes containing the digonal axes. Thus, the assemblage of a normal paraffin in the modified form now described can present tetragonal symmetry; the orientations of the succeeding strata, each of

which is composed of a certain number of layers of the composition CH_2 with the terminal hydrogen spheres added, will then differ by

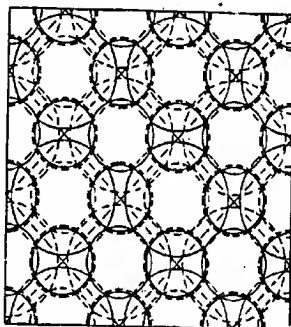
900. As remarked above, a section of a single stratum present in a butane assemblage is represented in Fig. 31.

That the marshalling of the assemblage of a normal paraffin, when of this altered form, is compatible with very close packing, is evidenced as before by the approach to a maximum of the number of contacts or close proximities round each sphere. Thus, each end carbon sphere of a chain is in contact with, or in close proximity to, six large spheres and fifteen small ones, together twenty-one, and each of the other large spheres is similarly environed by eight large and twelve small spheres, together twenty. Each terminal small sphere is environed by four large and four small spheres, and next to the terminal ones occur other small spheres immediately surrounded by five large and five small spheres: in the interior of the assemblage each small sphere is environed by six large and three small spheres. As before, the carbon spheres of a molecule containing several atoms form

a zigzag string; the angles of the zigzag are, however, much more obtuse in the form of assemblage now under consideration. The relation between the latter, which may be called the tetragonal assemblage, and the orthorhombic form of assemblage previously described, is indicated by stating that whilst the marshalling of the methylene portion is the same in both, the one is obtainable from the other by a general distortion

which alters the angles of the zigzag formed by the chain of carbon spheres, but does not appreciably alter the environment of the different spheres or the closeness of the packing; the molecular units are of a slightly altered form, although they retain much the same general configuration. In view of the indications obtained of the existence of alternative modes of partitioning, which do not give rise to observable tautomerism, in connexion with benzene (Trans., 1906, 89, 1696), and of such alternative modes which furnish a mechanism for the occurrence of tautomeric and isomeric change, it is very possible that a paraffin derivative which occurs in one form of assemblage throughout one range of temperature would undergo conversion into the alternative form on entering a different range of conditions.

FIG. 32.



Crystalline Form of Halogen Derivatives of Homologues of Ethane.

It will be convenient now to discuss the rather sparse crystallographic data available for the halogen derivatives of the homologues of ethane, and to show that these data are very closely and very simply related to the two forms of assemblage described above. The whole of the available goniometric data are dealt with under this heading.

$\beta\beta\gamma\gamma$ -Tetrabromobutane, $\text{CH}_3\cdot\text{CBr}_2\cdot\text{CBr}_2\cdot\text{CH}_3$, is dimorphous, and exists as a tetragonal and an orthorhombic modification, which have been measured by Fedoroff (*J. pr. Chem.*, 1890, [ii], 42, 145). The tetragonal form has the axial ratio $a : c = 1 : 1.28$; on stating this in the alternative tetragonal form of $a : c = \sqrt{2} : 1.28$, and multiplying the value of c/a by four, the number of carbon atoms in the open chain, the ratio becomes, when stated in the more convenient orthorhombic form:

$$a : b : c = 1.414 : 1.414 : 5.120.$$

The valency volume of this butane derivative is $V = 26$, and the equivalence parameters are thence calculated as:

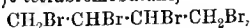
$$x : y : z = 1.929 : 1.929 : 6.985.$$

Since, in the tetragonal type of assemblage, the strings of carbon spheres which form the backbone of the molecules all have the same mean direction, symmetry would indicate that this is the direction of the axis c in the tetragonal crystal form now under discussion. The longer direction of the molecule having thus the direction of the parameter z , the dimensions of the fragment, CH_2 , in the crystal structure should be the above x and y and the fraction, $6/26$, of the above length, z . The equivalence parameters of the fragment, CH_2 , of the normal butane assemblage are thus calculated from the crystal form of the tetragonal modification of $\beta\beta\gamma\gamma$ -tetrabromobutane as

$$x : y : z = 1.929 : 1.929 : 1.612.$$

These values should represent translations in the tetragonal form of the general methylene assemblage; that they do represent such translations is shown by the manner in which they adapt themselves to the description of Fig. 31, in which they are marked. The orthorhombic modification of the substance is dealt with later (p. 2347).

The isomeric $\alpha\beta\gamma\delta$ -tetrabromobutane,



is described by La Valle (*Ber.*, 1886, 19, 572) as orthorhombic with $a : b : c = 0.9776 : 1 : 1.6820$, and is thus pseudotetragonal. Multi-

plying the ratio, c/b , as CH_4 ; if therefore a carbon sphere, which parameters for the whole substituted for a single close group of four with $W=6$ in the same manner, and will connect, four partial $x:y:z=1.947:1$ thus give a composite group of the $x:y:z=1.947:1$. Consequently, if throughout the

These values are not far removed close group of the composition H_4 , tetragonal isomeride; they suggest a carbon sphere substituted, in the present instance as compared as to make the relation of the slight compensatory approximation as a whole identical, such an direction of the axis c . A stereoisomorphism. There are two ways considered below (p. 2348). metrical manner, either

The tetrabromohexane of the constitution with the ascertained $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{C}$ is described by Negri (*Ber.*, 1889, 22, 2498) as α was under conditions: $a:b:c=0.3641:1:0.3788$, and is also pseudotification of the multiplying the length, b , by two, interchanging work composed calculating just as before the equivalence parameters for arrangement molecule, with $W=38$, and for the fragment, CH_2 , with packing the following values are obtained: tion of

$$\begin{array}{ll} x:y:z=1.830:1.956:10.329. & \text{With } W=38. \\ x:y:z=1.830:1.956:1.631. & \text{,, } W=6. \end{array}$$

These values for the methylene fragment approximate closely to those derived from the two previous cases.

The three halogen derivatives just above discussed thus present the tetragonal type of assemblage; the following appear to exhibit the alternative orthorhombic type first described, of which the halogen derivatives of ethane previously referred to afford examples.

As already noted, $\beta\beta\gamma\gamma$ -tetrabromobutane is dimorphous, and from Fedoroff's data for the orthorhombic modification Jaeger has calculated (*Trans.*, 1908, 93, 521) the axial ratios as $a:b:c=1.8671:1:3.478$. On multiplying the length b by four, the number of carbon atoms in the chain, interchanging b and c , and calculating the equivalence parameters for the whole molecule, with $W=26$, and for the methylene fragment, CH_2 , with $W=6$, the following values result:

$$\begin{array}{ll} x:y:z=1.868:3.479:4.000. & \text{With } W=26. \\ x:y:z=1.868:3.479:0.923. & \text{,, } W=6. \end{array}$$

From the mean values of the equivalence parameters for the halogen derivatives of ethane, namely, $x:y:z=1.967:3.396:2.149$, with the valency volume, $W=14$ (p. 2335), we obtain for the methylene fragment, CH_2 , with $W=6$, the values $x:y:z=1.917:3.396:0.921$; the value of z here is half that of the z of Figs. 17 and 18. This set of values approximates closely to that calculated from the data for the orthorhombic $\beta\beta\gamma\gamma$ -tetra-

Crystalline Form of Halogen Derivative, substance affects a form the orthorhombic ethane

It will be convenient now to discuss $\text{HBr}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, stereographic data available for the halogen ethane, and to show that these have been described by simply related to the two forms as crystallising in the mono- The whole of the available goes 6348: 1: 2: 3338, $\beta=80^\circ 55'$. On this heading, so that {101} becomes {100}, and

$\beta\beta\gamma\gamma$ -Tetrabromobutane, axial ratios are obtained in the form exists as a tetragonal and $\beta=82^\circ 58' 30''$; in these values a is have been measured by z is taken as a , and b is multiplied by four The tetragonal form axial ratios are thus obtained in the form this in the alternate 96: 4: 000, $\alpha=82^\circ 58' 30''$. The equivalence multiplying the whole molecule, with $W=26$, and for the fragment in the open chain $W=6$, are now calculated as before; the values convenient are

$$\begin{aligned} x:y:z &= 1.938: 3.316: 4.085. & \text{With } W=26. \\ x:y:z &= 1.938: 3.316: 0.943. & \text{,, } W=6. \end{aligned}$$

The latter set of values also agrees well with that derived from equivalent halogen derivatives of ethane, namely, with $x:y:z=17: 3.396: 0.921$.

The Secondary and Tertiary Paraffins.

The discussion of the configurations of the normal paraffins in the previous pages has revealed a singularly close correspondence between the customary method of representing the constitution of such substances and the conception of their configurations derived from the geometrical application of close-packing to assemblages of spheres of two volumes in the ratio of 4: 1. It has yet to be shown that the correspondence extends to the secondary and tertiary hydrocarbons of the same series.

Tetramethylmethane ($\beta\beta$ -Dimethylpropane), $\text{C}(\text{CH}_3)_4$.

The most obvious method of arriving at the assemblage representing tetramethylmethane consists in replacing each hydrogen sphere in the methane assemblage by the methyl radicle, CH_3 , in accordance with the second geometrical property; the discovery of the precise arrangement of the assemblage is, however, attended with much difficulty if this mode of procedure is adopted. Another method, which is more readily traceable, depends on the application of the first geometrical property to the methane assemblage, and may be thus described.

It has been pointed out that the four hydrogen spheres associated to form a close group in a methane assemblage belong to four

different molecular groups, CH_4 ; if therefore a carbon sphere, which is quadrivalent, be substituted for a single close group of four hydrogen spheres, it will belong to, and will connect, four partial groups or radicles, CH_3 , and thus give a composite group of the required composition, $\text{C}(\text{CH}_3)_4$. Consequently, if throughout the methane assemblage every fourth close group of the composition H_4 , selected symmetrically, is removed, and a carbon sphere substituted, this being done in such a manner as to make the relation of the units so obtained to the assemblage as a whole identical, such an assemblage will furnish a possible solution. There are two ways of accomplishing this in a highly symmetrical manner, either of which would appear to be in harmony with the ascertained facts.

When the structure of the methane assemblage was under consideration, it was pointed out that the shape and orientation of the groups, H_4 , influence the form of the skeleton framework composed of the carbon spheres, the reason of this being that the arrangement affected by these spheres must be such as gives the closest-packing of the groups in the cavities containing them; the substitution of single carbon spheres for some of the H_4 groups will, on the same principle, involve some slight modification of the skeleton framework of carbon spheres. The precise nature of this change is difficult to trace, especially in the absence of crystallographic data; for diagrammatic purposes it is therefore better, in each of the two solutions of the problem, to employ the simple arrangement of the carbon spheres in as high a symmetry as the marshalling which they present is capable of, without attempting to depict the exact equilibrium conditions ultimately attained.

The simpler of the two arrangements possible for the substituted carbon spheres has cubic symmetry. Thus, let the points of a certain cubic space-lattice indicate the centres of the carbon spheres of a methane assemblage; the centres of the cubes outlined by the system form a second similar space-lattice and mark the positions of the tetrahedral hydrogen groups. One-fourth of the groups can be selected for removal and substitution by additional carbon spheres in such a way that their arrangement is that of the unhatched cubes indicated in Fig. 33 *a* and *b*, which gives the two projections of the two sets of alternate layers. The alternative arrangement is a simple tetragonal one, and is shown in Fig. 34; this diagram is identical with Fig. 4, with the exception that every fourth cavity, symmetrically selected in tetragonal symmetry, is occupied by a carbon sphere. The newly introduced carbon spheres are shown as broken line circles, and are arranged contiguously in one of the three axial directions, namely, that perpendicular to the

plane of the figure; the groups of hydrogen spheres, H_4 , fill the strings of cavities marked A, which are not occupied by the added carbon spheres. Thus, the complete assemblage, much as in the case of benzene previously described (Trans., 1906, 89, 1693),

FIG. 33a.

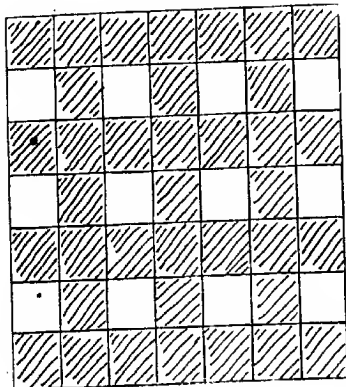
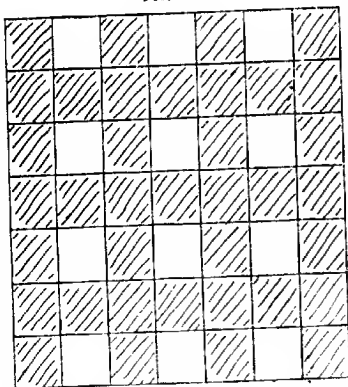


FIG. 33b.



of tetramethylmethane as thus derived is identical with that indicated by the theory of van't Hoff and Le Bel. The three hydrogen spheres attached to each methyl carbon atom will lie, as in methane, one in each of three out of four tetrahedrally situated cavities surrounding each methyl carbon sphere; the hydrogen

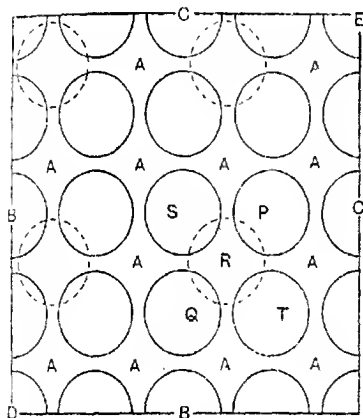
consists of continuous columns of carbon spheres in contact, the interstices between which are filled with groups of hydrogen spheres so arranged as to produce close packing; the columns consist of square groups of four separated by single carbon spheres throughout.

In both the cubic and the tetragonal assemblage described, the most symmetrical way of partitioning the system of carbon spheres into groups of five is to make these groups tetrahedral with the substituted spheres at the centres. Thus, in Fig. 34, the sphere R can be associated with P and Q of the four above, and with S and T of the four below, the four spheres P, Q, S, and T thus presenting a tetrahedral arrangement about the sphere R. The disposition of the carbon spheres in the molecule

spheres will follow, as closely as possible, the original arrangement prevailing in the methane assemblage.³

Inspection of Fig. 34 shows that the tetragonal assemblage for tetramethylmethane, like the first described, must approximate closely to cubic symmetry. The correctness of the mode of arriving at the arrangement which is here adopted is confirmed by Jaeger's determination of the crystal form of the tetrabromo-derivative of the hydrocarbon, namely, $C(CH_2Br)_4$; this author has shown, as

FIG. 34.



already indicated, that the substance is pseudo-cubic, being monosymmetric with the axial ratios, $a:b:c=1.0484:1:0.9472$, $\beta=90^\circ 45'$ (Trans., 1908, 93, 520).

Trimethylmethane (isoButane), $CH(CH_3)_3$.

It has been seen that the appropriate symmetrical intercalation or excision of methylene layers, CH_2 , effected in the case of a given normal paraffin assemblage produces some other normal paraffin assemblage; similar operations applied singly or in succession to the tetramethylmethane assemblage just described are productive of other assemblages appropriate to secondary or tertiary paraffins. The principle involved in such operations may be stated as follows. A regular layer of spheres, so constituted as to form the unit layer of a closest-packed assemblage of spheres, for example, a methylene layer, forms a constituent of some closest-packed assemblage. It is then found (α) that the two parts of this assemblage obtained by

the excision of this layer can close up and become closest-packed without any material rearrangement, and (b) that if, instead of removing this layer, the assemblage is divided so as to expose one of the faces of the layer, a second similar layer can be fitted on to this face and then the parts fitted up so as to form a closest-packed assemblage in which the added layer is intercalated.

The application of this principle depends on the property of an assemblage composed solely of such identical layers that some translation brings the contour of the adjoining portion of the assemblage which is fitted against one side of a single layer to coincidence with the contour of the other side of this layer, coupled with the fact that close-packing involves a close similarity of contour between all the surfaces of different sphere combinations which display the common property of fitting closely on to the same surface.

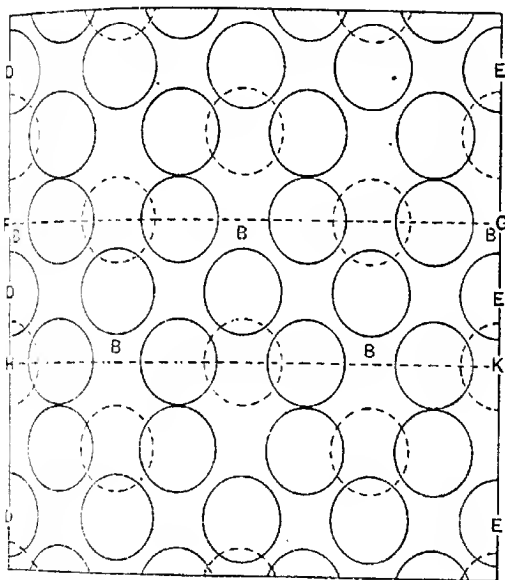
For the present purpose, isobutane or trimethylmethane, $\text{CH}(\text{CH}_3)_3$, may be regarded as derived by the removal of methylene, CH_2 , from the tetramethylmethane molecule. The possibility of performing this operation symmetrically on the tetramethylmethane assemblage, whether of the cubic form or of the tetragonal form represented in Fig. 34, constitutes a parallel between our method of formulation and the chemical relationship subsisting between the two hydrocarbons. The process is rather simpler as applied to the tetragonal form; this case may be described as follows.

One-fifth of the total number of carbon spheres in the tetramethylmethane assemblage are symmetrically removed, together with twice the number of hydrogen spheres, by withdrawing every fourth layer of the original carbon spheres taken parallel to a plane perpendicular to the diagram through a line DE in Fig. 34, together with the accompanying hydrogen spheres, and closing up the structure by bringing the exposed surfaces together. As the result of this operation, the skeleton assemblage depicted in Fig. 35 is obtained; it will be seen that, of the carbon spheres P, Q, S, and T, and the set of four, P_1 , Q_1 , S_1 , and T_1 , making up the eight carbon spheres which together enclose a substituted carbon sphere, only P, P_1 , Q, Q_1 , S, and S_1 survive, and that the new groups form two sets oppositely orientated in the resulting assemblage. In closing up the structure after removal of the methylene layer, a lateral shift is made, such a relative disposition of the opposing boundaries brought together being selected as brings the columns of carbon spheres at one boundary opposite to the strings of hydrogen spheres in the opposing boundary; this is possible because the central plane of the methylene layer in the original assemblage and the plane of the hydrogen spheres which becomes central in the modified

assemblage are alike capable of functioning as planes of gliding symmetry. The approximation of the portions fitted together, or the space gained by the excision, is treated as dependent on the postulate that the group of four hydrogen spheres occupies the same space in the assemblage as one carbon sphere; it follows from this that the CH_2 layer occupies three-fourths of the space required by a CH_3 layer.

The method described indicates roughly the relation of the

FIG. 35.



required assemblage to that of tetramethylmethane, but the character of the marshalling in the arrangement derived is imperfectly defined; still less is the precise nature of the crystalline symmetry exhibited. The absence of crystallographic data for the halogen derivatives of *isobutane* leaves the symmetry in doubt, but it is possible to assign to the marshalling of tetramethylmethane a very simple form, from which an equally simple one for trimethylmethane can be derived.

In the absence of crystal data, much latitude is presented for the shape taken by a given marshalling, and naturally the mar-

shalling of an assemblage can be most readily investigated when in its simplest form. Although this form will not, in general, be

FIG. 36a.

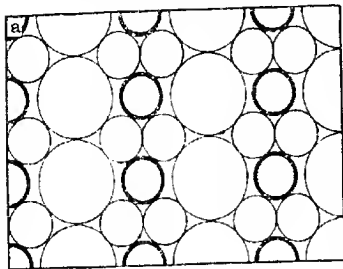


FIG. 36b.

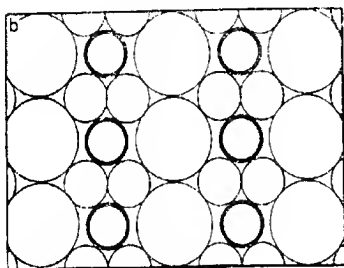
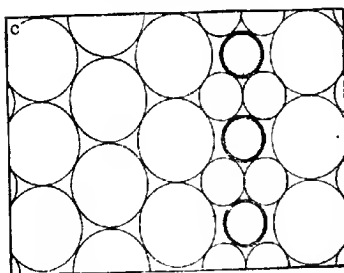


FIG. 36c.



the closest-packed one, it will approximate to the close-packed condition, and will display the property that every sphere will be in contact with, or in close proximity to, a large number of surrounding spheres. Now, the methane assemblage, without changing its general marshalling, can take the form depicted in Fig. 36 a and b; the simplest shape of the methylene layer, CH_2 , as depicted in Fig. 11, can here be recognised. Each layer of molecules, CH_2 , consists of the simple methylene layer with the additional hydrogen spheres symmetrically disposed in the same manner on both sides of it, as shown in the section *f*, the manner in which succeeding layers are fitted together in this simple marshalling is indicated by superposing *b* on *a* of Fig. 36. It must be clearly understood that the assemblage thus presented is not in its closest-packed form; it is a distortion of the closest packed assemblage above described of such a

nature as to simplify the internal symmetry without changing the marshalling. The methane assemblage, thus regarded, gives a configuration of the important radical CH_2 , which is

entirely in harmony with the symmetrical properties expressed by the graphic formulæ of the hydrocarbons. When it is employed as the root methane assemblage, the marshalling of the compound under consideration, and that of other kindred compounds, can be readily traced, and will be seen to be in accordance with the graphic formulæ.

The first step is to derive the corresponding simple form of marshalling for tetramethylmethane; this corresponds with the tetragonal type of the compound above indicated, and may be regarded as produced from it by a distortion. The process of derivation from the methane assemblage just described consists in substituting strings of carbon spheres for one-fourth of the strings of groups of the composition H_4 ; as a result of this change, the arrangement shown by superposing *b* on *a* of Fig. 36 becomes that obtained by superposing *c* on *a* of this figure. The layers shown on the plane of the diagram are the same as those found parallel to a plane drawn through DE perpendicular to the plane of Fig. 34.

The marshalling for trimethylmethane is obtained directly from that for tetramethylmethane by removing the central methylene portion from half the unsubstituted methane layers selected symmetrically and closing up the gaps, using the remnant hydrogen spheres in filling in between the parts of the assemblage which have to be fitted together after the excision. In the tetramethylmethane

FIG. 36d.

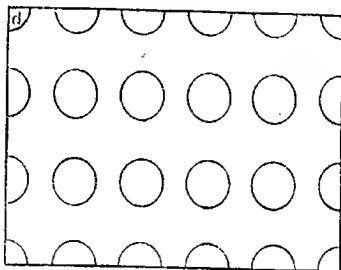


FIG. 36e.

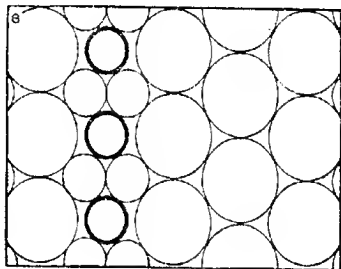
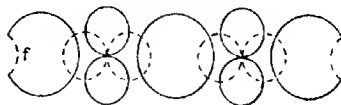


FIG. 36f.



assemblage, layers of the composition $\text{CC} + \text{CH}_4$ (Fig. 36c) alternate with layers of the composition 2CH_4 (Fig. 36a): the result of the excision described is to give a succession of sets of layers, $2\text{CH}_4 : \text{CC} + \text{CH}_4 : 4\text{H} : \text{CC} + \text{CH}_4$, etc., as represented roughly by superposing a, c, d, and e of Fig. 36.

The corresponding molecular unit is a combination of one carbon sphere from a layer a with the three carbon spheres of one of the two adjoining layers together with a due proportion of hydrogen spheres; the units are so constituted as to be all alike. With regard to the positions of the planes of gliding symmetry mentioned above, it is to be noted that in the tetramethylmethane assemblage the gliding plane is the median plane of layer a , and in the trimethylmethane assemblage it is the median plane of layer a or d ; these planes of gliding symmetry can be traced in Figs. 34 and 35 respectively. As already intimated, the nature of the adjustment of this marshalling which would be productive of the precise crystalline form remains unidentified owing to the absence of crystal data.

The geometrical process by means of which the trimethylmethane assemblage can be converted into that of tetramethylmethane is analogous to the process of preparing tetramethylmethane by the action of zinc methyl on *tert.*-butyl iodide.

Dimethylethylmethane (isoPentane), $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$.

If, in the derivation of the *isobutane* assemblage from that of tetramethylmethane, a layer of the general methylene composition, CH_2 , such as is excised from one side of the layer of tetramethylmethane complexes, is inserted in the symmetrical position on the other side of the layer, and the requisite shift of one layer on another made to close up the packing, the assemblage appropriate to *isopentane* or dimethylethylmethane results. The added layer has thus to be inserted on one side of each layer marked DE in Fig. 35. The relative situations of the two layers, CH_2 , thus placed together are indicated in Fig. 14; the relation of the composite layer formed to the remaining portion of the assemblage is shown in Figs. 34 and 35. The marshalling, as before, is represented in its simplest form.

Propane, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$.

If, in addition to the excision of the layers, DE, from the tetramethylmethane assemblage of Fig. 34 a set of layers, BAAC, parallel to them and symmetrically situated, is similarly removed and the exposed surfaces brought together as before, an assemblage is obtained which has the composition of propane. It is possible so to partition the assemblage thus obtained as to derive molecular

units of the form already indicated for propane (p. 2334); this is most readily shown in connexion with the original tetramethylmethane assemblage of Fig. 34.

In the propane unit described in connexion with the normal paraffins, the central carbon sphere makes four tetrahedrally situated contacts with surrounding spheres, two with carbon and two with hydrogen spheres, and of the four tetrahedrally situated contacts of each end carbon sphere, one is with a carbon and three with hydrogen spheres. Now in the tetramethylmethane assemblage referred to, each central carbon sphere makes four tetrahedrally situated contacts with carbon spheres, and when the withdrawal of parallel strata occurs, two of the four outer carbon spheres and four hydrogen spheres are removed from each molecular group. And as the removal of the carbon spheres reveals hollows on the surfaces exposed, formerly occupied by these spheres, which, when the closing up takes place, are occupied by hydrogen spheres projecting from the opposing similar surfaces, it is evident that the central carbon sphere of each group is, after the process, surrounded by four spheres, two of each kind tetrahedrally arranged. Further, it can be shown that each end carbon sphere, as in the tetramethylmethane assemblage, has tetrahedrally situated contacts with a carbon sphere and three hydrogen spheres. Thus, the hydrogen spheres remaining of a methane stratum, from which the central CH_2 layer has been removed, are left embedded in the two faces exposed, half in each; they consequently retain the same positions relatively to the end carbon spheres of the group found in the stratum to which they are attached. The same is true of the hydrogen spheres centrally placed in the stratum containing the end carbon spheres. Consequently, each end sphere of a group has the same tetrahedrally arranged contacts with a single carbon sphere and three hydrogen spheres after the excisions are made, just as it had before. It is therefore established as above stated that the two propane assemblages, that of the ordinary paraffin structure and that derived from the tetramethylmethane assemblage, can be partitioned into unit groups of the same form; in other words, they are polymorphous arrangements of the same molecular groups. The geometrical process, inverse to that indicated above, by means of which the second kind of propane-assemblage can be converted into that of tetramethylmethane, is analogous to Friedel and Ladenburg's conversion of $\beta\beta$ -dichloropropane, $(\text{CH}_3)_2\text{CCl}_2$, into tetramethylmethane by the action of zinc methyl.

The graphic formulæ for all the hydrocarbons of the general molecular composition $\text{C}_n\text{H}_{2n+2}$ can be derived from those of methane, trimethylmethane, and tetramethylmethane by the intro-

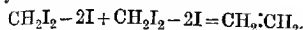
duction of methylene groups, CH_2 , into the formulae in all the ways consistent with the quadrivalency of carbon. It has been shown in the foregoing pages that close-packed assemblages of the general composition of the paraffins can be constructed which correspond in constitution and configuration with the normal hydrocarbons of the series; it has also been shown that other assemblages may be derived which possess geometrical properties exactly representative of the simple secondary and tertiary paraffins by means of simple substitution processes which closely parallel the modes of preparation of these hydrocarbons. The mode in which the geometrical substitutions are made renders it clear that similar operations appropriately performed will lead to the production of an assemblage corresponding in constitution with any primary, secondary, or tertiary paraffin. The conclusion must thus be drawn that the continued prosecution of the method described for deriving assemblages representing the paraffins must lead to a complete parallel between the possibilities of our geometrical method for interpreting atomic space arrangement and the variety of chemical processes of derivation which are so completely pictured with the aid of the ordinary graphic formulae.

The Olefinic Hydrocarbons.

The results obtained by means of the above method of deriving close-packed assemblages, which represent in composition, constitution, and configuration all the primary, secondary, and tertiary paraffins, have been shown to accord with all the available geometric data; although this evidence is small in amount, it appears to be of a very direct character. The assemblages for the normal paraffins are characterised by being built up wholly from the general methylene assemblage by the intercalation of additional hydrogen spheres in appropriate ways. It will now be shown that the reverse process, namely, the removal of hydrogen spheres from the general methylene assemblage, gives rise to a geometrical feature corresponding with the element of chemical constitution described as an ethylenic double bond. By the application of this process of excision to paraffinoid assemblages, fresh assemblages can be derived representing all the open-chain olefines of the general composition C_nH_{2n} , and it will further be demonstrated that peculiarities of configuration, which arise naturally during the process, represent the properties associated with the *cis*- and *trans*-isomerism of certain ethylene derivatives.

The formation of an olefine may be represented by the chemical operation of removing two hydrogen atoms from one terminal carbon atom of each of two paraffin molecules, and allowing the two

bivalent radicles thus obtained to condense, forming a hydrocarbon molecule containing an ethylenic double bond; this corresponds with the production of ethylene by the action of copper on methylene iodide, and may be thus formulated:



It has been shown that the orthorhombic and the tetragonal forms of the general methylene assemblage are capable of interconversion

FIG. 37a.

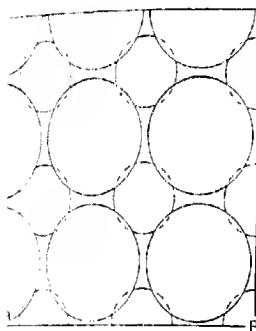
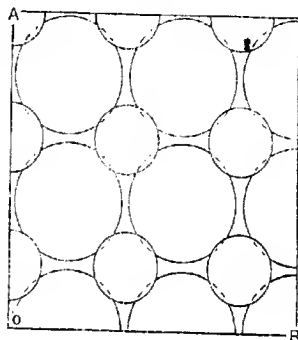
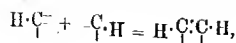


FIG. 37b.

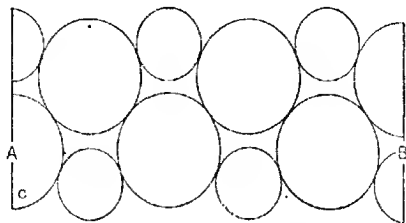


by means of simple adjustment without any violent rearrangement. The described process of excision may be applied to either form, but the tetragonal one lends itself the more readily to its application; it is the one the employment of which leads to a result that can be checked by crystallographic data, whilst that of the orthorhombic form at present does not. The application of the process to the tetragonal form of the general methylene assemblage alone is given here; the treatment of the other form is not attempted, first, because it is not at the moment of practical importance, and secondly, because the first step in the derivation of an olefinic form from an orthorhombic paraffinoid form may possibly consist in the passage of the latter to the tetragonal form.

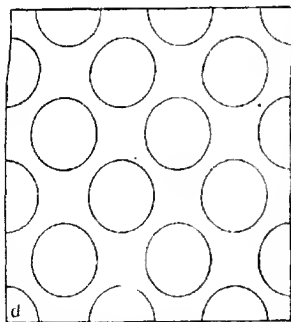
The configuration of the ethylenic grouping, as it presents itself in a homogeneous close-packed assemblage, is deduced by removing from a face of each of two composite layers, CH_2 , of the general methylene assemblage of the tetragonal form, the small spheres lying in the hollows of the face, and by then keying together the two faces thus laid bare. The process itself parallels that which may be thus formulated:



and is depicted in Fig. 37 *a* and *b* by superposing *b* on *a*; the section of the resulting assemblage of radicles through a line AB is given in Fig. 37*c*; it is concluded that the presence of such a double stratum as this is characteristic of an olefine. The only addition requisite to the stratum just described to produce from it the

Fig. 37*c*.

arrangement for ethylene is the appropriate insertion of spheres of valency volume 1 at each of its faces in the manner already described in connexion with the normal paraffins; the close-packed assemblage composed of the strata thus completed is obtained by arranging a succession of the strata of Fig. 37*c* with a layer of the

Fig. 37*d*.

small spheres between each of them, such as is shown in Fig. 37*d* (compare Fig. 33). In view of the comparative simplicity of this process, it will be convenient at once to demonstrate its application to a specific case in which a slight complicating adjustment accompanies the formation of the assemblage.

Jaeger has described tetraiodoethylene, C_2I_4 , as crystallising in the monosymmetric system with

$$a : b : c = 2.9442 : 1 : 3.4387,$$

$\beta = 70^\circ 44' 30''$ (Trans., 1908, 93, 523). In this description it is convenient to change the indices 001, $\bar{1}01$, $\bar{2}01$, $\bar{1}11$, and 100 to 100, 203, 001, 263, and $\bar{2}03$ respectively; the introduction of the factor three in this connexion seems permissible in view of the pronounced pseudo-hexagonal character of the compound, and as a result of the change the indices become more symmetrically

distributed, although numerically somewhat more complicated. The axial ratios are then obtained in the form:

$$a : b : c = 1.0891 : 1.07360 ; \beta = 84^{\circ}3' ;$$

whence the equivalence parameters are calculated, with $W=12$, as:

$$x : y : z = 2.689 : 2.469 : 1.817 ; \beta = 84^{\circ}3'.$$

The assemblage appropriate to tetraiodoethylene, and also there

FIG. 38a.

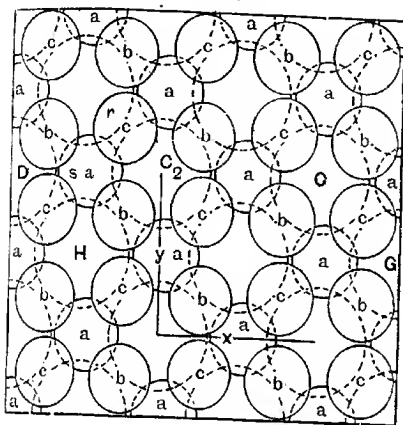
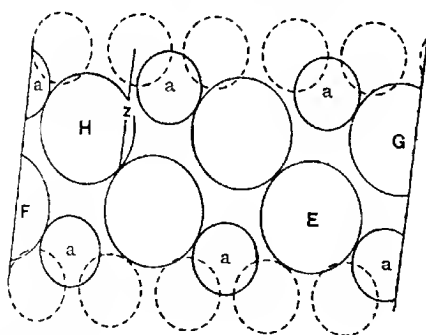
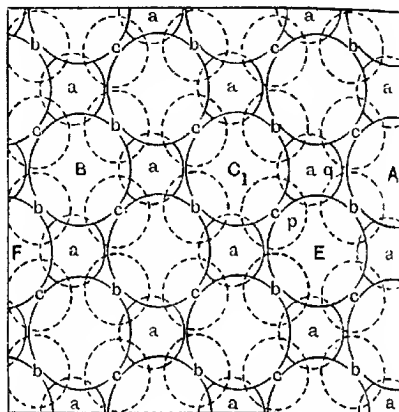
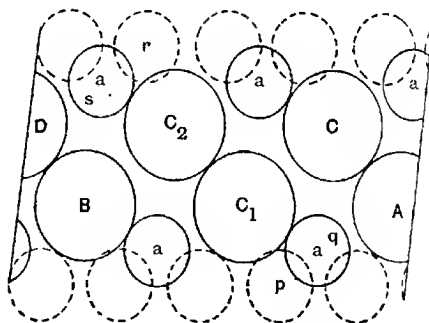


FIG. 38b.



fore to ethylene itself, is constructed on the basis of these values in the following manner. Carbon spheres are arranged in square order so as to be equidistant in the same plane, and nearly in contact, as in the general methylene assemblage of tetragonal form depicted in

Fig. 29; the squares are then converted by a distortion into rhombs, the diagonals of which are in the ratio of $x:y$. The arrangement and dimensions of the system thus produced are indicated by the large circles of Fig. 38*a*. On one face of the layer of carbon spheres are now placed spheres of volume 1, representing hydrogen or iodine,

FIG. 39*a*.FIG. 39*b*.

one in each of the hollows. If the arrangement of the large spheres were a square one, each small sphere would touch four large ones, as shown in Fig. 37; as it is, each small sphere makes but three contacts, and symmetry requires that these shall be such that the centres of

the small spheres display the same relative arrangement as the large ones, and are thus equidistant. Their situations are indicated by the circles marked *a* in Fig. 38*a*. The principal hollows now present on the face of the composite layer to which the spheres *a* have been added are just twice as numerous as the carbon spheres; they are next occupied symmetrically by other spheres of volume 1, as shown by the circles *b* and *c*. The block thus obtained can be regarded as consisting of three layers of spheres, one of large and two of small ones.

A second block of spheres similar to the first is now formed and the two blocks put together, so that the faces on which no small spheres have been placed fall together and key into one another, each large sphere of one block making contacts with three large spheres of the other block. Three contacts of large spheres are so made that the shift of the large spheres on the face of the block has the opposite direction to the shift of the small spheres, *a*, first placed on the other face. The relative situations of the two blocks are shown by superposing Figs. 38*a* and 39*a*, when it is seen that the system formed has diagonal axes parallel to the direction *y* passing through points of contact of carbon spheres; sections of the double layer of two blocks by two planes perpendicular to those of Figs. 38*a* and 39*a*, through the lines AB, CD and EF, GH respectively, are shown in Figs. 38*b* and 39*b*. Double blocks of the form thus obtained are fitted together in such a manner that the end layer of small spheres, *b* and *c*, of one block serve as the end layer of the next double block; thus, if the spheres *b* are allotted to one double block, those marked *c* are to be allotted to the adjoining one.

The composition of the completed assemblage corresponds with that of ethylene or tetraiodoethylene, and its dimensions, *x*, *y* and *z*, are the equivalence parameters above derived for the latter substance. It will be seen that the assemblage differs merely by a slight adjustment and a sheer equivalent to the angle $\beta = 84^\circ 3'$ from the more symmetrical one constructed to represent ethylene in which the carbon and hydrogen spheres are in square arrangement. It is interesting to note that the plane directions with the somewhat complex indices given above are found to be very important directions in the assemblage when their traces are drawn on the plan and section here given.

The fact of the limitation of the number of derivatives of the normal paraffins led van't Hoff to ascribe freedom of rotation to a singly bound carbon atom; a limitation of this kind does not obtain in the case of a doubly bound carbon atom, although the accepted graphic representation of the altered molecule and its derivatives is capable of a diagonal rotation by means of which it could be

represented. This discrepancy points to the loss of some symmetrical feature due to the presence of the double bond. An examination of the effect on a normal methylene assemblage of the removal of the double layer of hydrogen spheres and the closing of the gap, which, it is suggested, expresses the change referred to, shows that a deterioration of symmetry has supervened; strings of carbon spheres are not continued in the same planes across the plane at which the modification occurs, but a side shift or "fault" is necessitated in order that the two denuded surfaces may fit closely together. It is suggested that the existence of this break in the regularity of the strings of carbon spheres makes two different orientations equally available for the portion of an assemblage lying beyond the surface of modification; in other words, whilst in the case of a normal paraffin assemblage of the tetragonal form the addition of a layer, in order to give equilibrium, must be so performed that the joined layers have the same orientation, in the case where a double or ethylenic bond is present, it is equally favourable to equilibrium whether the two layers coming together have the same orientation or differ in orientation by 90° . The parallel which thus exists between the properties of close-packed assemblages and the occurrence of *cis*- and *trans*-isomerides amongst the derivatives of ethylene will be treated immediately in connexion with the isomerides of the composition C_4H_8 .

It should be remarked that the existence of the alternative referred to for the attachment of an added layer is inoperative in the case of ethylene, and in the cases of compounds equally symmetrical, such as tetraiodoethylene; in all such cases the two resulting forms become identical, and thus indicate, as they should do, that there is but one kind of molecule. The alternative becomes operative, however, in some derivatives of this simple form, since partial substitution of the hydrogen spheres allows two kinds of partitioning to be discriminated which are not interchangeable without re-marshalling. The effects of the presence of the structure represented by the ethylenic bond, as exhibited in cases of homologues of ethylene, will now be traced.

The Homologues of Ethylene.

After having traced a peculiarity of geometrical structure in a close-packed assemblage which corresponds with the double bond present in the ethylene molecule, it is desirable to ascertain whether the introduction of this geometrical feature into a paraffinoid assemblage leads to the production of the type of assemblage specifically associated with the presence of an ethylenic bond. For this purpose, it is convenient to consider the four butylenes, C_4H_8 .

which may be regarded as derived from butane and *isobutane* by the removal of two hydrogen atoms from the molecule; these substances are (1) *cis-s*-dimethylethylene, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}:\text{C} \\ \diagdown \\ \text{H} \end{array} < \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array}$, (2) *trans-*

s-dimethylethylene, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}:\text{C} \\ \diagdown \\ \text{H} \end{array} < \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$, (3) ethylethylene (butylene),

$\text{C}_2\text{H}_5\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, and (4) *as*-dimethylethylene (*isobutylene*),

$(\text{CH}_3)_2\text{C}:\text{CH}_2$. Further, in order that the possibilities of close-

packing under the specified condition of unit composition may be exhausted, as also those of isomerism of the molecular composition C_4H_8 , it will be convenient to discuss the assemblages representative

of the remaining two hydrocarbons of the latter composition, namely, (5) tetramethylene (*cyclobutane*), $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} > \text{CH}_2$, and (6)

methyltrimethylene (methylcyclopropane), $\text{CH}_3\cdot\text{CH} < \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} >$.

It will now be shown that the process of excising hydrogen spheres which has been applied above for the purpose of deriving the assemblage representing ethylene can be applied in three different ways to the normal butane assemblage; these lead to the production of three distinct assemblages, which represent the butylenes, numbered (1), (2), and (3). A similar process applied to the *isobutane* assemblage leads to the formation of an assemblage, which represents the asymmetrical dimethylethylene, numbered (4). In connexion with the analogy existing between the geometrical mode of representation employed and the possibilities of chemical isomerism, it will be shown that these four methods of applying the process of excision are the only ones that lead to the production of the geometrical peculiarity of structure corresponding with the presence of an ethenoid double bond; three other modes of excision are, however, also applicable, two to the butane assemblage, and one to that of *isobutane*; all of these result in the formation of assemblages which do not contain the ethenoid peculiarity of geometrical structure. Of the latter assemblages, two are identical and represent methyltrimethylene (6), which is derived both from the butane and the *isobutane* assemblage; the remaining assemblage is that of (5), tetramethylene, and is derived only from the butane assemblage. Since assemblages representative of the four homologues of ethylene and the two polymethylenes, which constitute all the isomerides of the composition C_4H_8 , are derivable from those representing the only two hydrocarbons of the composition C_4H_{10} by processes entirely analogous to the chemical methods of preparing the former hydrocarbons, strong confirmation is afforded of the general accuracy of the mode of formulation now put forward. These cases illustrate in a striking manner the geometrical property to which has been

ascribed the persistence of the tetrahedral disposition of the atomic links when substitution occurs; they consequently throw light on the precision with which the ordinary formulæ indicate the number and nature of the isomerides obtainable in any particular case.

The three modes of excision applicable to the assemblage representing normal butane for the purpose of deriving assemblages representative of the butylenes (1), (2), and (3) are the following. In a stratum of the normal butane assemblage of the tetragonal form, four attached layers of the composition CH_2 , and of the square configuration, are present; to each of the terminal faces of the block an appropriate set of hydrogen spheres has been added, as already explained (p. 2336). The stratum indicated is first divided at the median plane, so that each half consists of two layers of the form CH_2 , to one of

FIG. 40a.

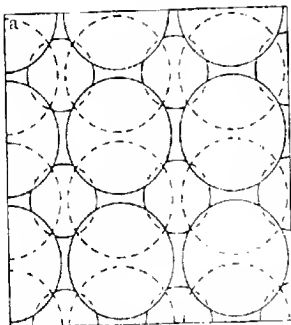
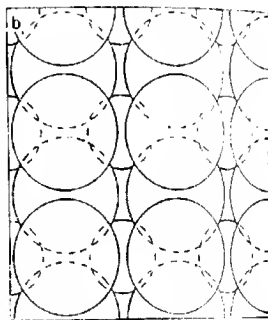


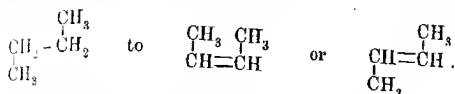
FIG. 40b.



which an additional set of hydrogen spheres has been added. From the surface of each of the two halves exposed by the separation the small spheres are now removed, and the two halves are then refitted together, making the large spheres of one face fit into the hollows of the other; this operation may be performed in two ways, one being represented by superposing *b* on *a*, and the other by superposing *c* on *a* of Fig. 40. In these diagrams the groups fitted together are of the form $\begin{smallmatrix} -\text{C}-\text{C} \\ | \\ \text{H} \end{smallmatrix}$, all the hydrogen spheres attached

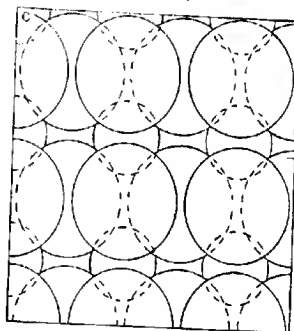
to the outer layer of carbon spheres—those representing the methyl hydrogen atoms—being omitted for the sake of clearness. The superposition of *b* on *a* gives the assemblage corresponding with *cis-s*-dimethylethylene, and that of *c* on *a* the assemblage for the *trans*-isomeride. No hydrogen spheres lie between the two deuded layers of carbon spheres fitted together as described, and the hollows

on the denuded surfaces from which the hydrogen spheres have been removed are now occupied by the carbon spheres of the opposing face. The geometrical operation which has thus been performed upon the normal butane assemblage may be roughly represented diagrammatically by the following scheme:



The assemblage of (3), ethylcethylene, is derived from that of normal butane by dividing the latter at the place of either the first or third linking so as to give as one segment a single layer of the form CH_2 , with its additional small spheres attached to one face only, and, as the other segment, a block or stratum of three layers, CH_2 , with the additional small spheres attached to one of its boundary faces. As before, the small spheres are removed from all the hollows of the two faces exposed by the separation, and the surfaces are then refitted; this operation can only be performed in one way without destroying symmetry, or rather, the two most symmetrical ways of fitting the strata closely together to produce a continuous assemblage give identical results.

FIG. 40.

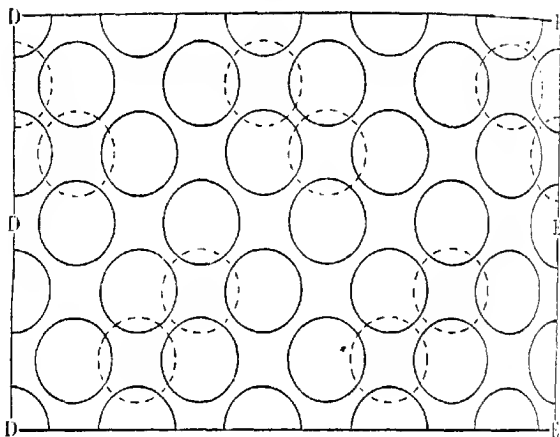


The assemblage for *as*-dimethylethylene (4) can be obtained from that of *isobutane*, but is most conveniently derived from that of tetramethylmethane, $\text{C}(\text{CH}_3)_4$, already described (Fig. 34), by removing from the latter one-half of the layers which have the composition H_2C , namely, either those whose median planes pass perpendicularly to the plane of the diagram through all the diagonal lines BC, or those whose median planes pass through all the lines DE. On removing the strata thus indicated and then re-fitting the denuded surfaces, a general arrangement is attained of which the large spheres alone are represented in Fig. 41; in this figure the removed layers of the composition H_2C are marked DE.

The three modes of excision which do not lead to the production of the geometrical feature corresponding with the ethenoid double bond remain to be dealt with; that which yields the assemblage

corresponding with (5), tetramethylene, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH}_2$, is next described. The assemblage for this hydrocarbon is derived from that of normal butane of the tetragonal form (Fig. 31) by removing the layers of hydrogen spheres which correspond with the terminal atoms in the paraffin chain, thus obtaining strata of the methylene form of assemblage, each consisting of four tetragonal layers of carbon spheres and the accompanying hydrogen spheres. Each stratum is next adjusted so as to bring its constituent carbon spheres close together in fours, as indicated diagrammatically in Fig. 42 *a* and *b*; the planes of these sections are perpendicular to those of

FIG. 41.



the tetragonal layers. The grouping is so performed that each four tetragonal layers of carbon spheres and attendant hydrogen spheres furnish two layers of tetramethylene complexes, as indicated by *a* and *b*. A single tetramethylene complex, plan and elevation of which are shown in Fig. 43 *a* and *b*, consists of four large spheres in the same plane and eight small spheres, four in each of two planes parallel to and equidistant from the plane of the carbon spheres.

The two remaining modes of excision applicable as already indicated (*a*) to the butane and (*b*) to the isobutane assemblage, lead to the production of the same molecular unit, that which represents methyltrimethylene; the former is applied to the normal butane assemblage of the orthorhombic form in the following manner.

(*a*) Alternate layers of the small terminal spheres of the normal

butane assemblage are removed as if for the purpose of condensing the strata in pairs so as to form strata of the normal octane

FIG. 42a.

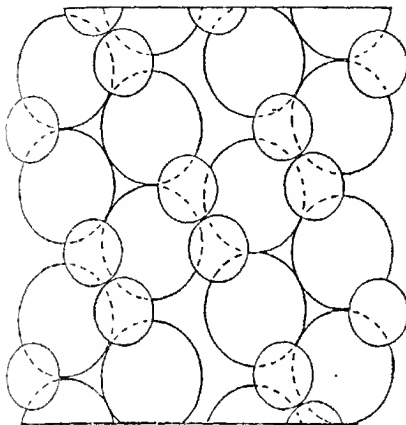
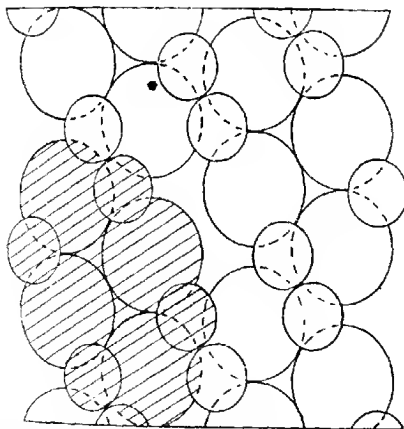


FIG. 42b.



assemblage, and each mutilated butane stratum is divided symmetrically into blocks of the composition CH_3 and $3(\text{CH}_2)$ respec-

tively. The latter blocks are next so adjusted that, as condensed together two by two, they form aggregates of trimethylene complexes arranged as is indicated by superposing *a* and *b* of Fig. 41; each stratum consists of six layers of large spheres as shown in the figure, and, as in the previous case, each small circle represents two spheres. Finally, one-half of the hydrogen spheres are removed symmetrically from the outer layers of the double stratum just described, and the outer layers are refitted to the CH_3 layers from which they were separated, the projecting carbon spheres of one face of the latter being allowed to fall into the hollows vacated by the hydrogen spheres last removed; simultaneously, the small spheres of the added CH_3 layers are adjusted for close-packing. The precise effect of the last process is difficult to trace, but its practicability is indicated by the facts that when the refitting has taken place, each sphere of the altered trimethylene layers is still immediately sur-

FIG. 43a.

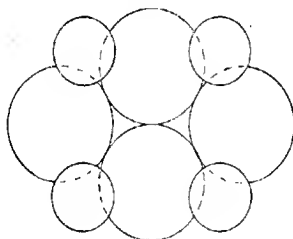
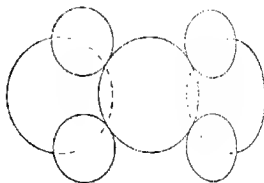


FIG. 43b.



rounded by the large number of spheres appropriate for very close packing, and that no destructive deformation of the original CH_3 arrangement is necessitated. The refitting of the layers is represented by the equation: $3(\text{CH}_2) - \text{H} + \text{CH}_3 = \text{CH}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ and

the assemblage attained is, as indicated by its constitution, composed of trimethylene complexes, from each of which a hydrogen sphere has been removed, grafted on to modified methyl complexes.

(b) A different assemblage of the same trimethylene complexes is derived from that of trimethylene by an appropriate excision of hydrogen spheres in the manner next described. In Fig. 35, representing the arrangement of the carbon spheres in the trimethylene methane assemblage, cavities and portions of cavities, which lie between two planes of which the traces are marked FG, HK, are available for the reception of hydrogen spheres; the central entire cavities are each of the magnitude requisite for the reception of

four hydrogen spheres, and the portions or half cavities have half this magnitude. Whilst maintaining the same configuration of the groups of four large

FIG. 44a.

spheres as is indicated in the figure, the two opposite sets are now allowed to approach until the cavities and portions of cavities afford only one-half the previous accommodation for hydrogen spheres; the effect of diminishing the accommodation offered by the cavities and portions of cavities to one-half the original amount is indicated in Fig. 45. Finally, without re-marshalling, such mutual adjustments are conceived as will adapt the various cavities between the large spheres to the close-packing of the appropriate numbers of hydrogen spheres; these adjustments will resemble, in general, those previously described in connexion with simpler cases.

The unaltered marshalling of the large spheres in each molecular group which is thus prescribed, and the advancement of large spheres to occupy cavities left vacant by the removal of the small ones, is fittingly represented by the transition from the graphic formula of trimethylmethane to that of methyltrimethylene immediately accomplished by removing a hydrogen atom from each

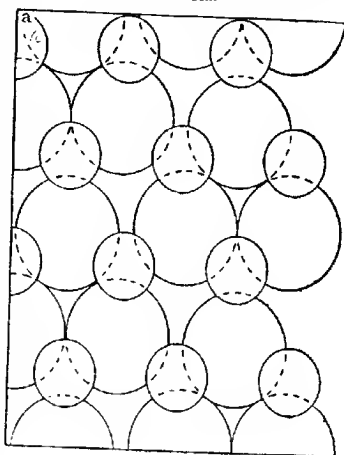
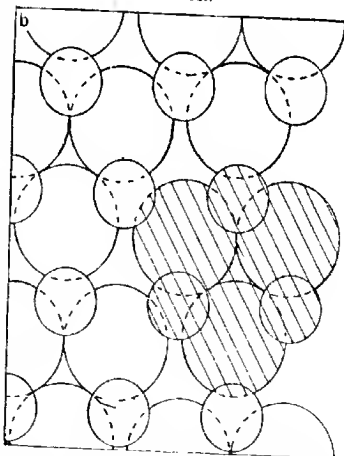


FIG. 44b.

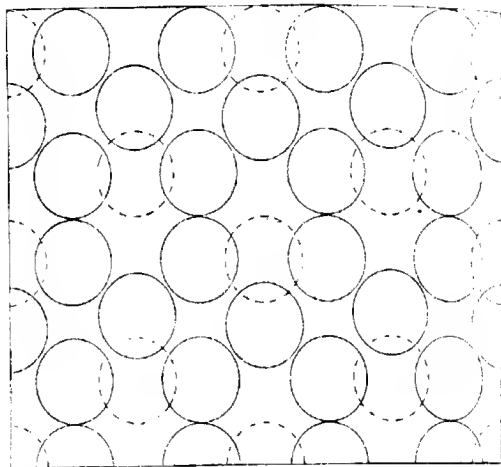


of two neighbouring branches of the molecule of the former, and restoring the linkage equilibrium by adding a link between the carbon atoms concerned, thus:



In connexion with the two methods just described for deriving

FIG. 45.



an assemblage representing methyltrimethylene, it is suggested that the course followed involves the initial formation and the subsequent preservation of an approximately regular tetrahedral disposition of the contacts of the carbon spheres with other spheres of the same molecular unit; the functional identity of the molecular units here indicated will necessitate that the two assemblages should be regarded as an example of polymorphism.

The arguments stated and the data given in the previous pages indicate that an ethenoid compound is derived from the corresponding paraffinoid compound by the removal of the requisite proportion of hydrogen spheres from the assemblage, and the subsequent contraction necessary to restore close packing to the assemblage. It would consequently be anticipated that pairs of substances of complex molecular constitution, the members of which differ in that a paraffinoid element, $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$, in the one is substituted by an

ethenoid element, $\cdot\text{CH}:\text{CH}\cdot$, in the other, might afford frequent instances of intimate crystallographic relationship; in such cases, the substitution just mentioned should occur in such a manner that the closing up of the assemblage would be manifested by a contraction in the direction of one of the properly selected equivalence parameters. Examples of this kind are not uncommon, and one may be here quoted.

Acenaphthene, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$, is morphotropically related to acenaphthylene, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix}$ (Billows, *Zeitsch. Kryst. Min.*, 1903, 37, 396); both belong to the orthorhombic system, and the axial ratios are respectively:

Acenaphthene, $a : b : c = 0.5903 : 1 : 0.5161$.

Acenaphthylene, $a : b : c = 0.5926 : 1 : 0.4996$.

The equivalence parameters corresponding with these axial ratios are:

Acenaphthene, $x : y : z = 3.3959 : 5.7527 : 2.9689$, $H' = 58$.

Acenaphthylene, $x : y : z = 3.4017 : 5.7404 : 2.8678$, $H' = 56$.

Differences $-0.0058 + 0.0123 + 0.1011$.

It is observable that the differences between corresponding equivalence parameters for the two substances are negligibly small in the directions x and y , but appreciably large in the direction of z ; in this case the replacement of the paraffinoid by the ethenoid structural element has involved a closing up of the crystalline assemblage, which is only experimentally appreciable in the direction of the c or z axis. An equally striking example is afforded by the morphotropic relationship observed between dibenzyl and stilbene, which is referred to later (p. 2379).

The Acetylene Series, $\text{C}_n\text{H}_{2n-2}$.

The space formation of spheres, which corresponds with the characteristic acetylene grouping, $\cdot\text{C}:\text{C}\cdot$, is rather more difficult to trace than that representing the double linking present in ethylene, but owing to the extreme simplicity of the molecular composition of the first member of the acetylene series, the possibilities to be submitted to consideration are so limited in number that examination of the arrangement to be described, which fulfils some of the principal conditions requisite, leaves practically no doubt that it is the one sought.

The assemblage representing acetylene itself is derived from a closest-packed cubic assemblage of spheres, each of the volume 4 (Fig. 1), in the following manner. Each of the large cavities in the assemblage, which are found at the centres of groups of six

spheres and are just as numerous as the spheres, is occupied by a smaller sphere of such magnitude as just to touch the six spheres enclosing the cavity; the assemblage represented in Fig. 46 is the

FIG. 46.

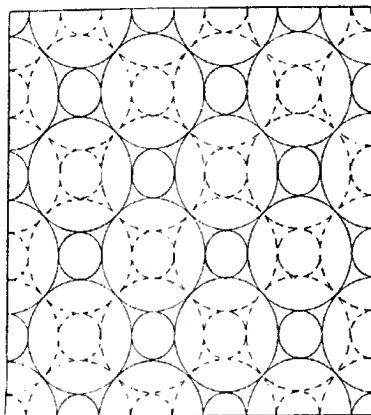
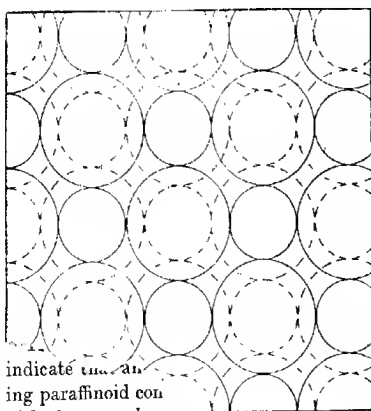


FIG. 47.



indicate the arrangement of hydrogen spheres

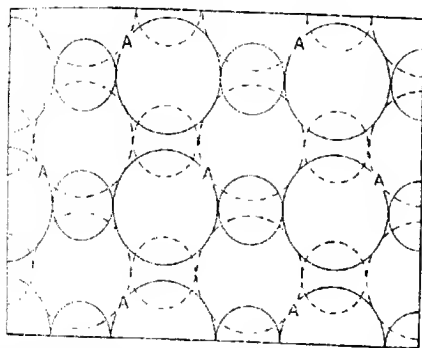
traction necessary for the continuous lines in Fig. 48. Let therefore the partners be so selected that the contacts of the paraffinoid elements

result. The smaller spheres which can thus be inserted are of a magnitude less than corresponds with the valency volume 1, and are next to be expanded until they attain this volume.

If the relative arrangement of the centres of both kinds remained unchanged during the expansion, it is evident that all the contacts between the larger spheres would be broken, as shown in Fig. 47, but it is possible for the large spheres to preserve some of their contacts, notwithstanding the presence of the smaller spheres, if slight mutual adjustment occurs. The assemblage can be regarded as composed of layers the planes of which are parallel to a plane drawn through opposite edges of a cube of the fundamental space-lattice; such a layer, viewed prior to the adjustment, is represented

of sphere with sphere are distributed through space as evenly as possible. The latter condition is fulfilled if the points of contact are approximately at the centres and angles of a cubic partitioning of space such that the length of a cube edge equals the translation of the assemblage along the directions in which carbon and hydrogen spheres are found placed alternately in contact. The assemblage thus modified consists of groups of a composition corresponding with acetylene, C_2H_2 ; the projections of the points at which the large spheres come into contact when the adjustment occurs are marked A in the diagram. The geometrical properties of the adjusted assemblage thus constituted parallel the chemical behaviour of acetylene, as will be perceived below in connexion with

FIG. 48.

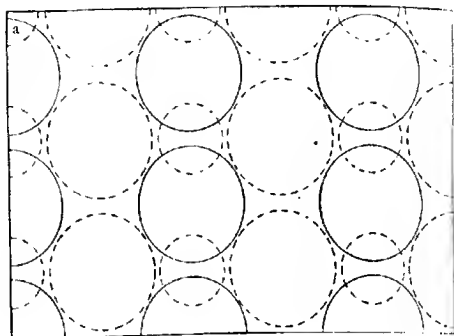
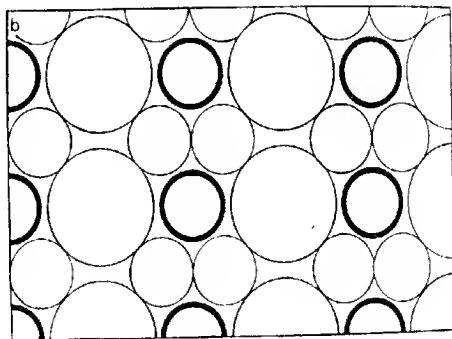


the homologues of the hydrocarbon. Owing to the fact that no crystallographic data are available for directly checking the geometrical results, the exact nature of the processes by which the succeeding terms of the acetylene series are arrived at, and the precise forms of the assemblages, are difficult to determine; the following is put forward, however, as the probable mode of deriving the correct form of assemblage for methylacetylene (allylene), $CH_3C\equiv CH$.

Methylacetylene (Allylene).

From one of the two similar faces of a layer of complexes such as is depicted in Fig. 48, the small spheres are removed, so that the residue represents the radicle, $\cdot C\equiv CH$; the stratum is then slightly thinned by diminishing its thickness and consequently increasing its face dimensions so as to make the latter equal to those of a layer

of the unadjusted orthorhombic ethane assemblage, Fig. 49*b*. On the denuded face of a stratum of this kind, which is shown in Fig. 49*a*, is next grafted a stratum of methyl complexes (Fig. 49*b*), namely, a half stratum of the ethane assemblage (Fig. 23); the process is represented diagrammatically by superposing Fig. 49*b* on Fig. 49*a*. The composition of the resulting compound stratum

FIG. 49*a*.FIG. 49*b*.

is represented by the formula $\text{CH}_3\cdot\text{C}:\text{CH}$, and the corresponding equilibrium assemblage will consist of a number of such strata keyed into one another; succeeding strata will be oppositely orientated, and the contacts between them will consequently be of two different kinds occurring alternately. One kind will resemble the terminal contacts found in the acetylene assemblage, as above presented.

and the other, those found in the normal paraffin assemblage of the orthorhombic form. As in most of the preceding cases, the marshalling described is represented in a simple form, and the

FIG. 50a.

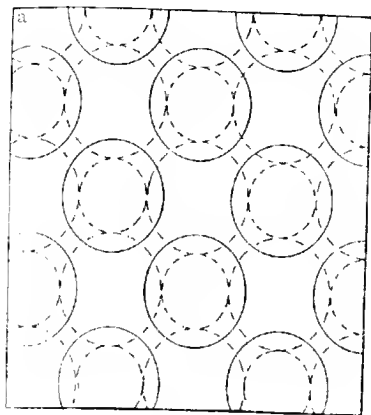
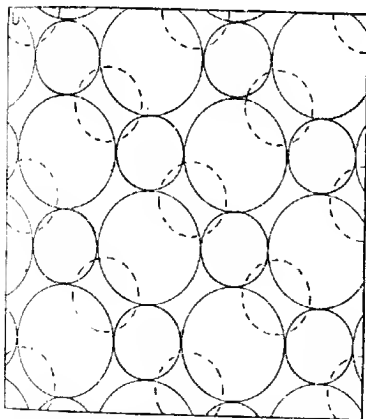


FIG. 50b.



assemblage must therefore be conceived to be subjected to such adjustment as is requisite to produce closest packing of this marshalling. It is important to observe that the assemblage just

described can be distorted so as to assume a tetragonal form without any considerable alteration of the environment of the constituent atoms; perhaps the simplest way of describing the result is to build up an assemblage from two kinds of tetragonal strata representing respectively the acetylenic remnant, $\cdot\text{C}\equiv\text{CH}$, and the methyl radicle, $\cdot\text{CH}_3$. The former is obtained from a tetragonal acetylenic layer (Fig. 47) by removing the hydrogen spheres from one of its faces, as shown by Fig. 50*a*, whilst the layer representing methyl is derived from the tetragonal ethane assemblage (Figs. 29 and 30), and its projection is represented diagrammatically in Fig. 50*b*. It is remarkable that in putting the two layers together the terminal face of the ethane stratum has in this case to be turned towards the denuded acetylene face, so that what was the inner face is now outwards; this is represented by superposing *b* on *a* of Fig. 50. The

FIG. 51.

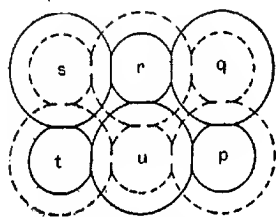
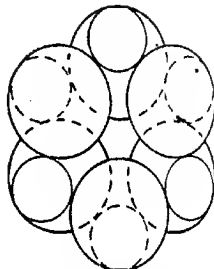


FIG. 52.



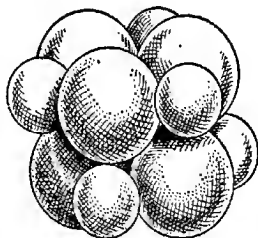
methylacetylene strata, $\text{CH}_3\cdot\text{C}\equiv\text{CH}$, as before, present opposite orientations in succeeding layers; in the tetragonal assemblage now being described, junctions, such as occur in acetylene, alternate with junctions having much the same marshalling as those of tetramethylmethane strata (p. 2348). The diagrams merely indicate the marshalling, and must be supposed subjected to adjustment which renders the packing closer.

The assemblage representing the next homologue of the series, ethylacetylene, $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, results from employing a butane stratum instead of an ethane one in the geometrical process described above.

It has been shown in the foregoing pages that the geometrical method indicates that the conversion of a paraffin assemblage into that of the corresponding olefinic and acetylenic hydrocarbon occurs by the excision of layers of hydrogen spheres, appropriately selected, in such a manner that the dimensions of the residual paraffinoid radicle suffer but little change. The paraffinoid, olefinic, or

acetylenic assemblage can, in fact, be regarded as consisting of a paraffinoid assemblage into which have been appropriately intercalated layers of the composition $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$, $\cdot\text{CH}:\text{CH}\cdot$, or $\cdot\text{C}:\text{C}\cdot$ respectively, these layers being dimensionally compatible with the paraffinoid part of the assemblage. In this dimensional compatibility between the three elements of constitution just mentioned is found a complete explanation of the frequent occurrence of close morphotropic relationships between corresponding paraffinoid, olefinic, and acetylenic compounds, and for which no cause has hitherto been traced. For the present it will suffice to quote the axial ratios for the monosymmetric dibenzyl, stilbene, and tolane as illustrating the relationship referred to (Boeris, *Zeitsch. Kryst. Min.*, 1901, **34**, 298):

FIG. 53.



| | $a : b : c$ | β |
|---|---------------------|---------|
| Dibenzyl, $\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Ph}$ | 2.0806 : 1 : 1.2522 | 115°54' |
| Stilbene, $\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{Ph}$ | 2.1701 : 1 : 1.4003 | 114 6 |
| Tolane, $\text{Ph}\cdot\text{C}:\text{C}\cdot\text{Ph}$ | 2.2198 : 1 : 1.3549 | 115 1 |

The Conversion of Acetylene Derivatives into Aromatic Hydrocarbons.

The assemblages just put forward as representing acetylene and its homologues have been constructed in accordance with the principles of close packing applied in numerous other cases, the existence of this condition consisting in the large number of spheres in contact with, or close proximity to, each sphere. Although uncorroborated to any considerable extent by crystallographic evidence, the correctness of the representation is strongly supported by the fact that the tetragonal assemblages described immediately provide a mechanism which can be shown to illustrate the well-known conversion of acetylene derivatives into aromatic hydrocarbons.

The acetylene assemblage has been derived from the closest-packed assemblage of equal spheres of the valency volume 4 by forcing spheres of valency volume 1 into the interstices which occur at the centres of close octahedral groups of six spheres and are as numerous as the large spheres. Before the insertion of the smaller spheres, the assemblage can be regarded as composed of identical groups of six spheres, and similarly, after the insertion of the hydrogen spheres, is built up of the composite groups of twelve spheres, six large and

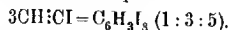
six small, depicted in Fig. 51. The latter groups, however, can be readily distorted into groups of the benzene configuration shown in Fig. 52, which has been previously described (Trans., 1906, **89**, 1693), and is shown in rough perspective in Fig. 53; this is easily seen by comparing Figs. 51 and 52. The acetylene assemblage of Fig. 48 can, consequently, be regarded as built up of units of the composition C_2H_2 , each representing an acetylene molecule, or as consisting of units of the composition C_6H_6 , each of which represents a distorted benzene complex.

The choice between the two kinds of partitioning can be expressed by the number of large spheres in immediate contact; if these touch two by two, while the pairs are not in contact but are kept apart by the smaller spheres, the acetylene grouping is indicated, but if the larger spheres form groups, each containing six carbon spheres in ring contact, each sphere of a layer of three being attached to two spheres of the neighbouring layer of three, the benzene configuration is portrayed. It is conceivable that the simpler form of grouping may give closest-packing when the ratio of the sphere magnitudes lies within certain narrow limits, and that when these limits are exceeded in one of the two directions, the other form of grouping may be brought about; the polymorphous forms of assemblage for benzene previously described would then follow from further change of the conditions. The passage from one grouping to the other above indicated will thus occur at some critical condition of temperature or the like; it involves no re-marshalling but some slight adjustment of the relative positions of the two sizes of spheres. The slight adjustment which is thus requisite to the conversion of the acetylene assemblage into an aggregate of units having the benzene configuration is the geometrical analogue of the conversion of acetylene into benzene by heat.

The acetylene assemblage, in accordance with our previous results, must be regarded as practically identical in form and relative dimensions with the assemblages of the halogen derivatives of the hydrocarbon; by replacing each hydrogen sphere in it by an iodine sphere of approximately the same valency volume, the assemblage representing the crystalline di-iodoacetylene would be obtained. Von Baeyer's observation (*Ber.*, 1885, **18**, 2269), that di-iodoacetylene, C_2I_2 , is converted into hexaiodobenzene by slight warming or the action of light, is in complete accordance with this.

A similar kind of mechanism elucidates the polymerisation which occurs when monoiodo- or monobromo-acetylene is preserved in the crystalline or dissolved state, and which leads to the production of the 1:3:5-tri-iodo- or tribromo-benzene respectively (von Baeyer, *loc. cit.*). For the representation of these changes, the hydrogen

spheres on one side only of the stratum of acetylene complexes are replaced by iodine or bromine spheres of approximately the same volume as hydrogen; the distortion of the assemblage for mono-iodo- or bromo-acetylene thus obtained leads to the re-partitioning in the sense of the equation:



The compound tetragonal assemblage for allylene, $\text{CH}_3\text{C}:\text{CH}$, depicted in Fig. 49, was obtained by the intercalation of two kinds of strata, those, namely, of the acetylene and methane radicles. Polymerisation strictly corresponding with that observed is brought about geometrically by altering the acetylene stratum just as in the previous case; the three carbon spheres of a newly constituted benzene complex thus formed, which lie in one of the two planes, become respectively attached to three methyl groups of the adjoining stratum so as to give the symmetrical constitution of mesitylene.

In the derivation of the assemblage for allylene, the hydrogen spheres on one side only of the acetylene layers were replaced by a layer of methyl complexes; if the hydrogen spheres on both sides of each acetylene layer are replaced by layers of methyl complexes, the assemblage produced represents that of the symmetrical dimethyl-acetylene (crotonylene), $\text{CH}_3\text{C}:\text{C}:\text{CH}_3$. The passage by slight distortion of the acetylene layers to the benzene configuration involves the conversion of each set of three dimethylacetylene complexes into one molecular complex of hexamethylbenzene in a manner precisely paralleled by the observed facts.

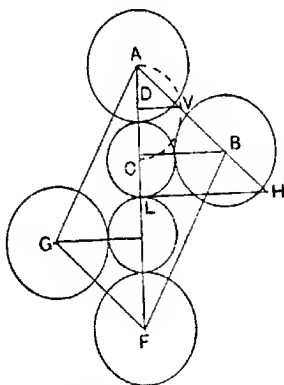
If oxygen spheres are introduced into the allylene assemblage described above in the proportion of one for each acetylene unit present, and two hydrogen spheres are simultaneously introduced for each oxygen sphere, in accordance with the second geometrical property, an assemblage is obtained which has a constitution corresponding with that of acetone, $\text{CH}_3\text{CO}\cdot\text{CH}_3$. The removal of the elements of water from this assemblage, so as to convert it into the allylene assemblage, accompanied by the slight distortion which causes the assemblage to pass to the benzene form, corresponds symmetrically with the observed conversion of acetone into mesitylene by the dehydrating action of sulphuric acid. The following method may be applied to the production of an assemblage for acetone, in which the process referred to can be readily traced.

The general methylene assemblage described above (p. 2326) can be distorted to an acute rhombohedral form without sensibly affecting the closeness of the packing; the volume of each rhombohedral unit cell, like that of the orthorhombic cell before described, is that proper for one radicle unit, CH_2 . The corners of the cell are occupied by the centres of carbon spheres, and the cell contains at

its centre a pair of hydrogen spheres, the pairs being similarly orientated. The resulting assemblage can be traced in the following simple manner. The assemblage may be regarded as consisting of similar layers of the same composition as the layers depicted in Fig. 19, the planes of centres being parallel to a plane drawn through the axis of a cell to contain one of the rhombohedral edges which intersect this axis; a constituent layer can be derived if the configuration of a single unit cell is ascertained in the following manner.

Two circles, centred at A and C, of which the diameters are in the ratios of those of the carbon and hydrogen spheres, are drawn in contact (Fig. 54); on the line joining the centres, AC, a semicircle, AVC, is erected, and AC is produced to cut the smaller circle in L. The line LH is drawn perpendicular to AL. AL is

FIG. 54.



trisected in D, and DV is drawn perpendicular to AL, to intersect the semicircle in V. A and V are joined, and the join produced to cut JH in J; VH is then bisected in B, and with B as centre a circle equal to circle A is drawn.

Since $AD = 1/3 AL$, $AV = 1/3 AH = VB$; therefore, since AVC is a right angle, $AC = CB$, and circle C, which touches circle A, also touches circle B. L is now used as a centre of symmetry, about which points, lines, and circles are symmetrically repeated, as shown in the figure; the

parallelogram ABFG is the section of a rhombohedron of the form required, and the circles centred at A, B, F, and G are the sections of carbon spheres of which the centres lie at those angular points of the rhombohedron which are intersected by the plane of the section depicted; the small circles indicated are the sections of hydrogen spheres enclosed, each having contact with the other and with three carbon spheres lying on one side of L in a plane perpendicular to AL, as well as with one carbon sphere of which the centre lies on this line. For, if the line ALF be made a trigonal axis, and by successive rotation through 120° about it, four other points are located from the points B and G while points A and F remain unmoved, the eight points thus

FIG. 55.

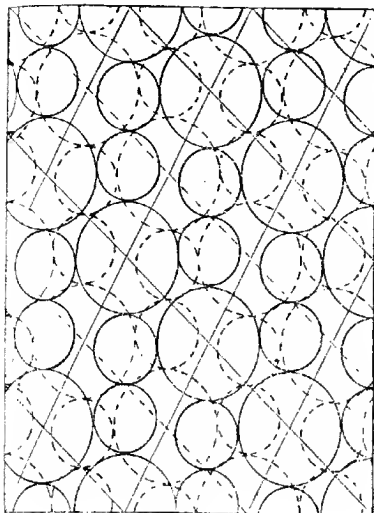


FIG. 56a.

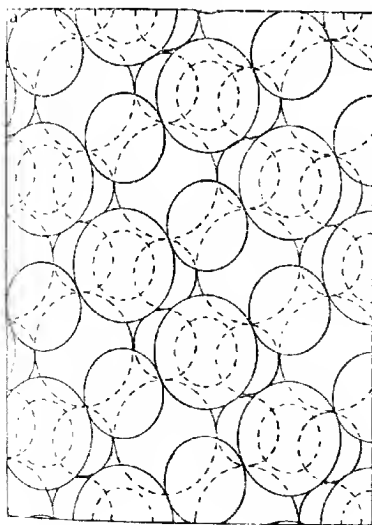


FIG. 56b.

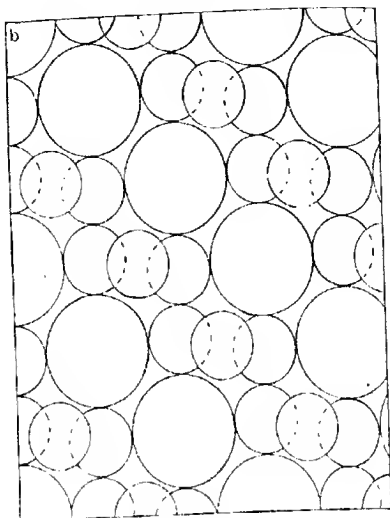
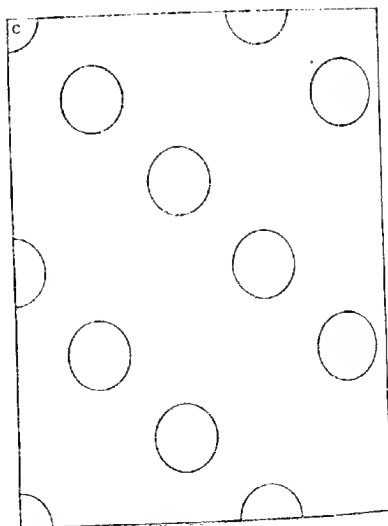


FIG. 56c



indicated are connected by the property that the six points not on the axis are equidistant from it and lie three and three on two planes which trisect the axis AF, a property characteristic of the angular points of a rhombohedron. The proof of the existence of this property lies in the fact that the traces of the planes referred to, being the horizontal lines through B and G, respectively trisect the semi-axes AL and FL.

When space has been partitioned by means of three sets of parallel equidistant planes into rhombohedra of the form indicated, and carbon spheres have been placed with centres at all the angles, while pairs of hydrogen spheres occupy the cell centres, each large sphere is in contact with eight small spheres and almost in contact with six large spheres, while each small sphere touches four large spheres and one small one. This kind of arrangement can be traced in Fig. 55, which shows layers constructed according to the cell conditions derived above; the continuous and discontinuous lines respectively depict projections of succeeding layers.

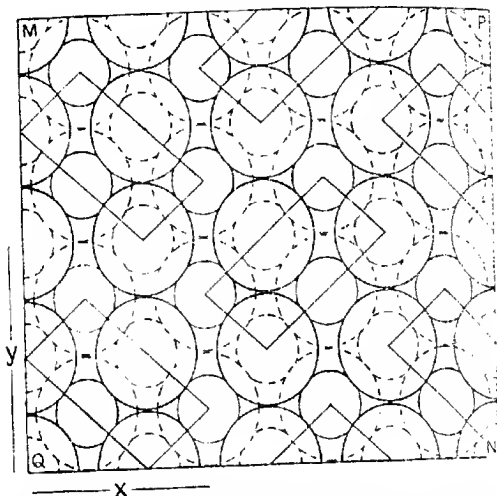
In order to derive from the methylene assemblage of the form thus described an assemblage for acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$, three succeeding layers are taken, and an oxygen sphere substituted for each pair of hydrogen spheres of the central layer of the three; this can be done without any sensible change in the form of the rhombohedral cell. A number of sets of three layers thus modified must then have hydrogen spheres added, just as in the case of the previously described methylene assemblage, so as to produce strata which appropriately represent the formula of acetone; the resulting assemblage in its most symmetrical condition is indicated by superimposing *b* on *a* of Fig. 56, *a* representing the two layers, CH_2 and O respectively, with the terminal hydrogen spheres added, and *b* representing a single layer, CH_2 , with its terminal hydrogen spheres.

Geometrical complexes of the composition OH_2 can be readily recognised in the assemblage described, each oxygen sphere being early in contact with four hydrogen spheres, two above and two below the plane of the layer. The withdrawal of the pairs of hydrogen spheres of one of the layers simultaneously with the oxygen spheres of the next layer, with which they are nearly in contact, deprives the middle carbon layer of all its smaller spheres, and leaves but one hydrogen sphere, namely, the end one, to be allotted to each of the carbon spheres of an end layer; this, when the assemblage is closed up after the extraction of the OH_2 complexes, leads to the marshalling above deduced for allylene, $\text{CH}_2\cdot\text{C}\cdot\text{CH}$, and subsequently the deformation already referred to converts the allylene assemblage into that proper for mesitylene (p. 2381).

A mechanism similar in kind to that explained and illustrated above is apparently applicable to the more complex cases presented by the various pyridine, quinoline, and quinaldine syntheses.

The geometrical simplicity of the operation by which the elements of water can be introduced into an acetylenic assemblage is completely paralleled by the ease with which acetylene, $\text{CH}\equiv\text{CH}$, reacts with water under the influence of a catalyst to yield acetaldehyde, $\text{CH}_3\cdot\text{CHO}$. In order to represent the assemblage corresponding with the latter substance, two of the layers of a methylene assemblage of rhombohedral form, as just described, are requisite, the

FIG. 57.



pairs of hydrogen spheres in one of the two layers being exchanged for single oxygen spheres. The appropriate addition of hydrogen spheres at the opposite faces completes a stratum corresponding with the constitution of acetaldehyde; the latter is represented by superposing *c* on *a* of Fig. 56.

In connexion with the distorted configuration (Fig. 51) just described as an intermediate form displayed by the benzene complex during its production from acetylene, it is significant that unit having this configuration can be fitted together to make an assemblage which is compatible with the axial ratios and crystalline form of benzene itself, but which is not identical with the benzene assemblage previously described (Trans., 1906, 89, 1694, Fig. 3). Th

somewhat remarkable fact that the same spheres present in the same proportions are capable of two widely different arrangements presenting almost the same crystalline form and axial ratios is traceable to the spheres occurring in continuous strings in two of the three axial directions; thus, in the earlier assemblage just referred to, the large spheres range in contact in the direction of the axis y , and large and small spheres alternately range in contact along the direction of the axis z . The dimensions y and z closely correspond, in fact, with twice the diameter of a carbon sphere and with the sum of the diameters of a carbon and a hydrogen sphere respectively; any assemblage in which carbon and hydrogen spheres range in this manner along directions of translations will consequently be morphotopically related to the benzene assemblage previously described. The assemblage of the distorted units of Fig. 51 is shown diagrammatically in Fig. 57, in which each of the parallelograms indicated marks the projection of the centre portion of a column of benzene complexes of which the axis is perpendicular to the plane of the figure; the sphere centres of each single molecular unit are projected on the outline of some one such parallelogram. The partitioning of this diagrammatic assemblage into molecular complexes can occur in several different ways, which produce identical results; the parallelograms are drawn appropriately for two of these ways, the column indicated by a single parallelogram being divisible into molecular units in two ways (compare Trans., 1906, 89, 1696). The values of x and y used in the construction of Fig. 57 are those calculated for crystalline benzene, in which

$$x : y : z = 3.101 : 3.480 : 2.780.$$

The assemblage shown in Fig. 57, being unadjusted, is equally applicable to acetylene and benzene; it shows neither of the kinds of coalition of spheres to form a complex which have respectively been described as productive of molecular units proper to these compounds. This accounts for the marked flattening of the spheres which is found to be necessary in order that they may be packed into the space accorded by the benzene valency volume of $V = 30$. In three directions in the assemblage, namely, one perpendicular to the plane of the diagram, and two, those of the diagonals MN, PQ, the large and small spheres alternate. In the diagram they are represented as precisely in line, but this will not be strictly the case, especially along the directions of the diagonals; increased closeness of packing, and therefore less flattening, will result from a slight zigzagging of the positions of the two sets of centres of the same string.

The conclusion referred to, that continuous strings of spheres are

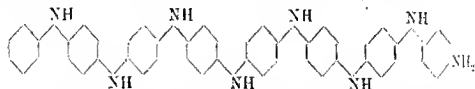
present in which the two sizes alternate, throws light on the numerous cases in which the value of the z axis for benzene is very approximately presented as one of the equivalence parameters of benzene derivatives; many such instances have been recorded by Jerusalem (*Trans.*, 1909, **95**, 1275) and by Armstrong (*this vol.*, p. 1578).

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CXXLIII.—*Aniline-black and Allied Compounds. Part I.*

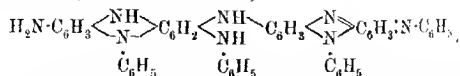
By ARTHUR GEORGE GREEN and ARTHUR EDMUND WOODHEAD.

ALTHOUGH the recent researches of Willstätter and his pupils (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; *J. Soc. Dyers*, 1908, **24**, 4; Willstätter and Dorogi, *Ber.*, 1909, **42**, 2147, 4118) have added much of value to our knowledge of the complex oxidation products of aniline, the constitution of aniline-black and of its intermediate products still cannot be regarded as completely elucidated. The view advanced by Willstätter, that these compounds are all to be regarded as indamine-like derivatives of the eight-nuclear chain compound (leucoemeraldine):



will scarcely gain acceptance without further evidence. As Bucherer has pointed out, it might a priori be expected that substances of such a type would exhibit a high degree of instability, and would readily decompose into simpler compounds under the influence of acids, etc.

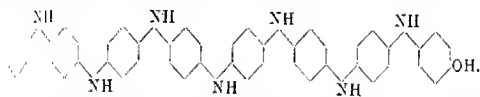
Amongst other arguments in support of the chain structure, Willstätter has shown that the quantitative conversion into *p*-benzoquinone is only compatible with the existence of di-*para*-connections, and is entirely opposed to an azine structure, such as that suggested by Bucherer (*Ber.*, 1909, **42**, 2931):



In respect to the validity of this argument, it is, however, necessary to point out that a sharp distinction must be made between the

primary oxidation products of aniline (emeraldine, nigraniline, etc.) and the condensation products of these with aniline ("ungreenable aniline black"), which latter alone can be properly regarded as true aniline black. Willstätter's experiments refer only to the former class of compounds, and it yet remains to be shown what yield of *p*-benzoquinone is obtainable from the latter. It is quite conceivable, and in fact probable, that whilst the former possess a di para chain or ring structure, the "ungreenable aniline-black," that is, true aniline-black, is an azine (Green, *The Chemical Technology of Aniline-black*, 7th Internat. Congress of Applied Chemistry, London, 1909; *J. Soc. Dyers*, 1909, 25, 188). Only the "ungreenable aniline-black" can be correctly regarded as a highly stable compound; the primary oxidation products probably owe much of their apparent stability to their insolubility in water and aqueous solvents, for when dissolved in pyridine, etc., they exhibit a much greater tendency to undergo change.

The view held by Willstätter that "ungreenable aniline-black" is a compound of the same type as the primary oxidation products—that is, contains an eight-nuclear chain, and only differs from the primary products in the degree of oxidation and the replacement of the terminal NH by O), is opposed, in our opinion, to the experimental facts. Were this view correct, the behaviour with sulphurous acid of the two oxidation stages he describes should be the same, that is to say, both compounds should be reduced to the green monoquinonoid stage, and by the application of a stronger reducing agent all should be reduced to the mother substance, that is to the oxygen analogues of leucoemeraldine:



Furthermore, this reduction-product, like leucoemeraldine itself, would certainly be a tolerably stable substance, giving, on air oxidation, only the lowest quinonoid stage, and requiring the application of a strong oxidising agent to reconvert it into the original tri- or tetra-quinonoid compound. These properties are not exhibited either by the preparations described by Willstätter as "hydrolysed triquinonoid and tetraquinonoid blacks," or by the "ungreenable aniline-black" produced on the fibre. The latter is not reduced at all by sulphurous acid, and by stronger reducing agents such as hyposulphites, it is converted into a leuco-compound which is rapidly re-oxidised by air to the original "black," and that apparently without passing through any lower stage of oxidation. Moreover, the facts known respecting the conditions of

formation of "ungreenable aniline-black" clearly show that it cannot be a product of further oxidation alone, but is a condensation product with aniline of a different type to the simpler oxidation products from which it is formed (Green, *loc. cit.*).

In order to throw more light on this complicated subject, it has appeared to us necessary to obtain, in the first instance, further evidence for the molecular weight and constitution of the primary oxidation products (emeraldine and nigraniline), and we have attempted to do this by determining, on the one hand, the quantity of hydrogen required to reduce these products to leucoemeraldine, and, on the other, the quantity of oxygen necessary to oxidise each stage into the next. The data obtained in this manner, combined with the fact that we have been able to recognise four distinct stages of oxidation of leucoemeraldine, support Willstätter's view of an eight-nuclear molecule, but do not agree with the constitution assigned by Willstätter and Dorogi to the compounds they prepared.

Assuming the correctness of the eight-nuclear structure for the primary oxidation products, it still remains an undecided question whether the aniline residues are to be regarded as united in an open or in a closed chain, but without attempting to decide this point we shall make use of the open-chain formulae to express provisionally the analytical results. The constitution of "ungreenable aniline-black" we reserve for discussion in a later communication.

Before proceeding to a consideration of the results obtained, it is desirable to attempt to clear up some of the existing confusion regarding the various oxidation products of aniline and their nomenclature. Much of the obscurity in this subject arises from the fact that no criterion of purity has hitherto existed, and that the products obtained have been doubtless largely mixtures. Unsuitable nomenclature has still further added to the confusion. Thus the name "emeraldine," which properly belongs to the first acid-oxidation product of aniline—a violet-blue base giving green salts, and well known to dyers of aniline-black—has been transferred by Willstätter and Moore to an entirely different compound, namely, the blue imide obtained by polymerisation of phenylquinonedimide, which was apparently first mistaken for emeraldine by Caro. On the other hand, for the true emeraldine, originally so-called by Crace-Calvert and Lowe, the name "triquinonoid aniline-black" is now proposed by Willstätter and Dorogi, although emeraldine is neither black nor (as will be shown later) is it triquinonoid. In justification for this confusing and unnecessary transfer of names, Willstätter and Dorogi advance the incomprehensible plea that "technisches Emeraldine längst nicht mehr existirt."

The various oxidation products which have been described under the name of aniline-black by the earlier authors (Müller, Nietzki, Kayser, Gayard, etc.) are lacking in any criterion of purity or individuality beyond that furnished by elementary analysis, which in this case is quite inconclusive and valueless. The discovery that the primary oxidation products (emeraldine and nigraniline bases) are readily soluble in somewhat diluted organic acids, such as 80 per cent. acetic acid and 60 per cent. formic acid (the former base giving a green solution, and the latter a blue), whilst the higher condensation products are insoluble in these solvents, has provided us with a valuable means for diagnosis and separation, by means of which we have been able to show that all the above-mentioned so-called "aniline-blacks" consist mainly of emeraldine and nigraniline mixed with varying proportions of higher condensation products. These "blacks" prepared in substance therefore do not properly correspond with the aniline-black produced on the fibre, since in the latter case the higher condensation products are either exclusively present (ungreenable blacks) or largely predominate (greenable blacks).

In order to simplify the nomenclature, we propose that the term "aniline-black" should be restricted to the higher condensation products (ungreenable black), whilst the original names "emeraldine" and "nigraniline" should be retained for the primary oxidation products. As, however, there is a stage of oxidation below emeraldine and one above nigraniline, we propose for these the names "protoemeraldine" and "pernigraniline." All four substances, protoemeraldine, emeraldine, nigraniline, and pernigraniline, are quinonoid derivatives of the same parent substance, to which we have given the name "leucoemeraldine." Into this compound they are all converted on reduction, and from it they can all be produced by oxidation. At present the protoemeraldine stage has only been obtained in the *o*-toluidine series, whilst pernigraniline is too unstable to isolate in a dry state.

Emeraldine.

This compound is the first clearly defined stage in the oxidation of aniline in an acid medium, whatever the oxidising agent employed. When a chloride is used, the reaction tends in part to at once proceed further with production of more or less nigraniline, but with hydrogen peroxide, if not used in excess, the oxidation stops at the emeraldine stage. If the reaction is effected in the cold and in the presence of an excess of acid, emeraldine and nigraniline are nearly the sole products, but if the mixture is neutral or only slightly acid, a certain quantity of condensation products (ungreen-

able black) is also produced. An excess of acid is therefore a necessary condition for preparing emeraldine in a pure state. As the result of a series of experiments, proportions corresponding with 1 mol. of aniline hydrochloride to 1.33 mols. of oxygen and 1 mol. of hydrochloric acid were found the most suitable.

Emeraldine is also produced by the further oxidation of the blue imide, $C_6H_5NH \cdot C_6H_4NH \cdot C_6H_4N \cdot C_6H_4NH$, of Willstätter and Moore (termed "emeraldine" by these authors).

I. A solution of 100 grams of aniline hydrochloride, 42 grams of sodium chlorate, and 46.5 c.c. of hydrochloric acid (33 per cent. HCl) in 1800 c.c. of water, to which 2 drops of syrupy vanadium chloride are added, is kept in the cold for from two to three days. The precipitate is then collected, washed thoroughly with water, basified by mixing the paste with dilute ammonia in a mortar, finally washed with alcohol and with water, and dried at 35–40°. The product thus obtained contains a varying amount of nigraniline, which may be readily converted into emeraldine by warming the precipitate with dilute hydrochloric acid before basifying. Pure emeraldine may also be obtained by dissolving the crude base in 50 parts of 80 per cent. acetic acid, filtering from any insoluble matter, reprecipitating by addition of dilute hydrochloric acid, collecting the hydrochloride, and finally basifying the precipitate with ammonia. During this process the nigraniline present is converted into emeraldine.

II. A solution of 50 grams of aniline hydrochloride in $\frac{2}{3}$ litre of water, to which is added 135 c.c. of hydrochloric acid (33 per cent. HCl), 380 c.c. of hydrogen peroxide solution (4.6 per cent. and 0.5 gram of ferrous sulphate, is kept in the cold for twenty-four hours. The precipitated emeraldine is collected, washed, and basified with ammonia.

III. Ten grams of *p*-aminodiphenylamine are dissolved together with 27 c.c. of hydrochloric acid (33 per cent. HCl) in 1 litre of water. After cooling to 0–5° by addition of ice, 78 c.c. of hydrogen peroxide (4.7 per cent.), followed by 0.1 gram ferrous sulphate, are added. The hydrogen peroxide used was rather more than twice the quantity required to convert the aminodiphenylamine into Willstätter and Moore's blue imide. On adding the iron salt, a voluminous indigo-blue precipitate of the imide was first produced, which, after about twelve to twenty-four hours, slowly lost its blue colour and became green, while the excess of peroxide disappeared and an odour of *p*-benzoquinone was apparent. The mixture was warmed on the water-bath, and the precipitate collected, washed, and basified with ammonia.

When prepared by either of these methods, the emeraldine base

forms an indigo-blue powder, which, when purified by the acetic acid method, has a bronzy lustre. When dried at a low temperature it retains a remarkably large amount of water (about 30 per cent.). It is insoluble in alcohol, benzene, chloroform, etc., but dissolves readily in cold pyridine, giving a bright blue solution. This solution is, however, very unstable, for in a short time the greater part of the product separates out again as a colloidal precipitate. This precipitate consists of a condensation product of quite different properties to the original emeraldine. In concentrated sulphuric acid, emeraldine dissolves with a reddish-violet colour, and on addition of water a bright green precipitate of the sulphate is obtained. Towards acetic and formic acids the behaviour of emeraldine and nigraniline is very remarkable. These bases are insoluble in glacial acetic acid or in concentrated formic acid, and are also insoluble in these acids when fairly dilute, but in acids of medium concentration, that is, in acetic acid of about 80 per cent. or in formic acid of about 60 per cent., they dissolve readily. The solutions obtained with emeraldine are yellowish-green, and give a green precipitate on the addition of mineral acids or salts. By means of such a solution, the various stages of oxidation can be very effectively demonstrated, for on addition of a very dilute solution of chromic acid the green colour of the solution first changes to pure blue (nigraniline), and then, as more oxidising agent is added, to violet (pernigraniline), finally giving a violet precipitate (pernigraniline chromate). If to the violet solution of the pernigraniline a very weak solution of sodium hydrogen sulphite is added, these colour changes occur in the opposite direction, namely, from violet to blue, and from blue to green. Stronger reducing agents, such as phenylhydrazine, sodium hyposulphite, or titanium trichloride, convert emeraldine into leucoemeraldine.

In order to determine the quantity of hydrogen required for conversion of emeraldine into leucoemeraldine, the acetic acid solution was titrated with titanium trichloride according to Knecht's method, the analysis being carried out as follows. One gram of emeraldine in fine powder is weighed into a 250 c.c. flask containing 10 c.c. of water, and well shaken to prevent any of the powder glomerating into lumps. Glacial acetic acid is then added until the flask is about three-quarters full, the contents well shaken, and heated on the water-bath for fifteen minutes to about 90° to ensure conversion of all nigraniline present into emeraldine. The solution is then cooled, and made up to the mark with glacial acetic acid. For each titration, 25 c.c. of this solution (=0.1 gram of substance) are transferred, by means of a pipette, to a conical flask, and mixed with 25 c.c. of water and a measured excess of titanium

trichloride, the strength of which is re-determined each day. The mixture is kept in the cold for ten to fifteen minutes, air being excluded by a slow stream of carbon dioxide. At the end of this time the solution is quickly filtered from the precipitated leuco-emeraldine, employing a funnel and filter paper enclosed in a vessel filled with carbon dioxide. An aliquot portion of the whole (50 c.c.) is then transferred to another flask also containing carbon dioxide, and at once titrated with a standard ferric alum solution, employing ammonium thiocyanate as indicator. In calculating the results, the percentage of water, chlorine, and ash is allowed for, and a further small correction, determined by parallel blank experiments made under exactly the same conditions, is introduced for the loss of titanium trichloride oxidised by air during the operation. The first preparation analysed (obtained by method I) contained 31.9 per cent. of water, 1.1 per cent. of chlorine, and 0.1 per cent. of ash. The following results were obtained:

| No. of experiment. | Vol. of TiCl_3 run in, c.c. | Vol. of TiCl_3 unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Hydrogen value of 1 litre TiCl_3 , gram. | Percentage of hydrogen on pure dry emeraldine. |
|--------------------|--------------------------------------|--|---|---|--|
| 1 | 25 | 13.70 | 1.77 | 0.0374 | 0.533 |
| 2 | 25 | 14.15 | 0.92 | 0.0366 | 0.543 |
| 3 | 25 | 11.15 | 0.92 | 0.0366 | 0.543 |
| 4 | 25 | 13.23 | 1.30 | 0.0358 | 0.540 |
| 5 | 25 | 13.65 | 1.34 | 0.0358 | 0.536 |
| 6 | 25 | 13.55 | 1.33 | 0.0353 | 0.542 |
| 7 | 25 | 13.47 | 1.29 | 0.0358 | 0.545 |
| 8 | 25 | 13.47 | 1.29 | 0.0358 | 0.545 |
| | | | | Mean..... | 0.543 |

A second series of estimations was made with a larger excess of titanium trichloride and another preparation of emeraldine containing 30.65 per cent. of water, 1.0 per cent. of chlorine, and 0.1 per cent. of ash. Using 0.1 gram for each titration, the following results were obtained:

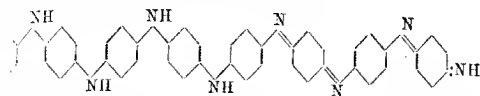
| No. of experiment. | Vol. of TiCl_3 run in, c.c. | Vol. of TiCl_3 unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Hydrogen value of 1 litre TiCl_3 , gram. | Percentage of hydrogen on pure dry emeraldine. |
|--------------------|--------------------------------------|--|---|---|--|
| 1 | 50 | 40.69 | 0.87 | 0.0442 | 0.547 |
| 2 | 50 | 40.59 | 0.87 | 0.0442 | 0.553 |
| 3 | 50 | 40.80 | 0.88 | 0.0442 | 0.540 |
| 4 | 50 | 40.69 | 0.87 | 0.0442 | 0.547 |
| | | | | Mean..... | 0.547 |

Figures of the same order were also obtained by direct titration of the acetic acid solution with titanium trichloride, although, owing

to the uncertain end-point, the results were not as trustworthy as those obtained by the indirect method.

The mean value of the two series of determinations was 0.545 gram of hydrogen for 100 grams of pure dry emeraldine.

A quinonoid compound of the formula:



would require 0.555 per cent. of hydrogen for complete reduction to the leuco-compound.

In order to estimate the quantity of oxygen consumed in the conversion of emeraldine into nigraniline, two methods have been adopted. The first consists in titrating an acetic acid solution of emeraldine with a standard solution of chromic acid until the pure blue colour of the uigraniline is reached. The second consists in separately titrating emeraldine and nigraniline until the violet pernigraniline chromate is completely precipitated. Deduction of the quantity of chromic acid required to reach this point for nigraniline from the quantity required to reach the same point for emeraldine gives the quantity consumed in oxidising emeraldine into nigraniline. Owing to the more definite end-point, the latter method is the more trustworthy.

I. Twenty-five c.c. of emeraldine solution, containing 0.1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 3.32 grams of chromium trioxide per litre (equal to 0.845 gram of oxygen per litre). The emeraldine employed contained 31.9 per cent. of water, 1.1 per cent. of chlorine, and 0.1 per cent. of ash and 1.5 c.c. of chromic acid (several experiments) were required to give a pure blue colour. Correcting for contents of water, chlorine, and ash, this is equivalent to a consumption of 1.9 grams of oxygen per 100 grams of pure dry emeraldine for oxidation to nigraniline.

II (a) Twenty-five c.c. of emeraldine solution, containing 0.1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 0.704 gram of chromium trioxide per litre (equal to 0.169 gram of oxygen per litre) until the precipitation of the violet pernigraniline chromate was complete, and no further change of colour took place. The emeraldine employed contained 30.65 per cent. of water, 1 per cent. of chlorine, and 0.1 per cent. of ash.

| No. of experiment. | Weight of emeraldine, gram. | Vol. of CrO_3 required, c.c. | Percentage of oxygen on pure dry emeraldine. |
|--------------------|-----------------------------|---------------------------------------|--|
| 1 | 0.1 | 24.5 | 6.07 |
| 2 | 0.1 | 25.0 | 6.19 |
| 3 | 0.1 | 25.0 | 6.19 |
| 4 | 0.1 | 24.5 | 6.07 |
| Mean..... | | | 6.13 |

(b) A weighed quantity of nigraniline (preparation see later) was added in a state of fine powder to 5 c.c. of water. The whole was cooled in ice, 20 c.c. of glacial acetic acid added, the mixture shaken until dissolved, and then at once titrated with chromic acid as above. The nigraniline employed contained 11.28 per cent. of water, 1.12 per cent. of chlorine, and 1.3 per cent. of ash:

| No. of experiment. | Weight of nigraniline, gram. | Vol. of CrO_3 required, c.c. | Percentage of oxygen on pure dry nigraniline. |
|--------------------|------------------------------|---------------------------------------|---|
| 1 | 0.0950 | 19.5 | 4.02 |
| 2 | 0.0983 | 20.0 | 3.98 |
| 3 | 0.1257 | 25.0 | 3.89 |
| 4 | 0.1017 | 21.0 | 4.04 |
| Mean..... | | | 3.98 |

Deducting 3.98 from 6.13 gives 2.15 as the percentage of oxygen required to oxidise pure dry emeraldine into nigraniline. If emeraldine has the above formula, it would require, theoretically, 2.20 per cent. of oxygen for the removal of two hydrogen atoms, that is, to introduce one quinonoid group.

Nigraniline.

The best method for the preparation of nigraniline in substance was found to be the oxidation of emeraldine base (or the mixture of emeraldine and nigraniline obtained by the chlorate oxidation), using an excess of hydrogen peroxide in an ammoniacal solution. For instance, the precipitate obtained by oxidising 40 grams of aniline hydrochloride and 18.6 c.c. of hydrochloric acid with 16.8 grams of sodium chlorate in presence of vanadium, as already described, is basified with ammonia, and the washed product, without being dried, is evenly suspended in 6 litres of water, to which 400 c.c. of hydrogen peroxide (3 per cent.) and 40 c.c. of concentrated ammonia are added. After keeping overnight, the precipitate is collected, washed well, and dried at 35°. The product contained 11.28 per cent. of water, 1.12 per cent. of chlorine, and 1.30 per cent. of ash.

Nigraniline base forms a bluish-black powder with a bronzy lustre. Like emeraldine, it is insoluble in most solvents, but dissolves in cold pyridine with a bright blue colour. The salts are blue, not dark green as stated in the literature. This error arises from the fact that nigraniline salts are very unstable, and both in substance and on the fibre are readily converted into salts of emeraldine. The change takes place slowly in the cold, but more rapidly on heating, and is accompanied by the production of *p*-benzoquinone. One part of the nigraniline is oxidised to *p*-benzoquinone, whilst another part is reduced to emeraldine, a fact which affords an explanation of the well-known "greening" of certain blacks on the fibre when exposed to an acid atmosphere. Similarly, when nigraniline is dissolved in concentrated sulphuric acid, it gives a violet solution of rather bluer shade than that of emeraldine, but on pouring into water, decomposition occurs, and a bright green precipitate of emeraldine sulphate is produced. Nigraniline dissolves readily and completely in cold 80 per cent. acetic acid or in 60 per cent. formic acid, giving pure deep blue solutions. These solutions, on warming, quickly change in colour to the green of the emeraldine salt. In contrast to the instability of the salts, nigraniline base is quite stable.

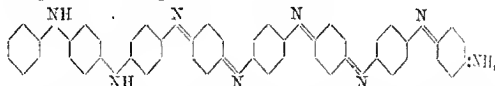
In performing the quantitative reduction of nigraniline, it is essential for the above reasons to avoid all heating in making the solution, and to effect the reduction as rapidly as possible. The operation is therefore carried out as follows. A weighed quantity of nigraniline (about 0.1 gram), which must be very finely powdered to ensure quick and complete solution, is suspended in 5 c.c. of water contained in a small flask. The flask is then cooled in ice for ten minutes, 20 c.c. of glacial acetic acid added, and the mixture shaken for half a minute, by which time the substance should have dissolved completely. Before the addition of the acetic acid, the air in the flask is expelled by carbon dioxide. The titanium trichloride solution is then added, and the titration effected in the same manner as with emeraldine:

| No. of experiment. | Weight of nigraniline taken, gram. | Vol. of TiCl_3 run in (1 litre = 0.0307 gram of hydrogen), c.c. | Vol. of TiCl_3 left unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Percentage of hydrogen on pure dry nigraniline. |
|--------------------|------------------------------------|--|---|---|---|
| 1 | 0.1009 | 40 | 17.3 | 0.87 | 0.771 |
| 2 | 0.0673 | 40 | 23.85 | 1.20 | 0.791 |
| 3 | 0.1059 | 40 | 15.62 | 0.73 | 0.772 |
| 4 | 0.1320 | 50 | 20.47 | 0.63 | 0.781 |
| 5 | 0.1198 | 50 | 23.38 | 0.72 | 0.770 |
| 6 | 0.1108 | 50 | 24.35 | 0.75 | 0.801 |
| Mean..... | | | | | 0.781 |

Another series of titrations made with a stronger titanium solution (1 litre = 0.0442 gram of hydrogen) gave the following results:

| No. of experiment. | Weight of nigraniline taken, gram. | Vol. of TiCl_3 run in (1 litre = 0.0307 gram of hydrogen), c.c. | Vol. of TiCl_3 left unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Percentage of hydrogen on pure dry nigraniline. |
|--------------------|------------------------------------|--|---|---|---|
| 7 | 0.1386 | 50 | 27.98 | 0.51 | 0.767 |
| 8 | 0.0900 | 50 | 35.06 | 0.68 | 0.416 |
| 9 | 0.1090 | 50 | 32.10 | 0.58 | 0.816 |
| 10 | 0.1035 | 50 | 32.95 | 0.60 | 0.816 |
| Mean..... | | | | | 0.811 |

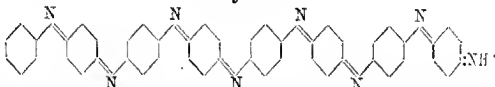
A triquinonoid compound of the formula:



would require 0.835 per cent. of hydrogen for complete reduction to leucoemeraldine. This formula is also supported by the oxidation numbers given under emeraldine.

Although the above formula is the same as that given by Willstätter and Dorogi to the preparation which they term "tri-quinonoid aniline-black," yet the compound described and analysed by them can scarcely be identical with nigraniline, for the properties do not correspond. If these authors originally had nigraniline in hand, it must have suffered conversion into emeraldine, and probably into further decomposition products by the process of purification employed.

Pernigraniline.



When a solution of emeraldine or nigraniline in acetic or formic acid is treated with an excess of a powerful oxidising agent, such as chromic acid or ammonium persulphate, the oxidation proceeds beyond the nigraniline stage, giving rise to a violet precipitate, which, on basifying with ammonia, yields a purple-brown compound, "pernigraniline." This substance is exceedingly unstable, decomposing slowly on drying, or even if kept in the paste form, with reproduction of nigraniline and formation of other products. This decomposition occurs still more rapidly in the presence of acids, following a similar course to nigraniline, which, together with *p*-benzoquinone, is first formed. The change is brought about by a few drops of dilute hydrochloric acid, and also more slowly by acetic acid. Reducing agents, if applied at once, convert per-

nigraniline first into nigraniline, then into emeraldine, and finally into leucoemeraldine. The base is soluble in pyridine, with a purple colour, and apparently undergoes decomposition in this solvent in the same manner as do emeraldine and nigraniline. In concentrated sulphuric acid, it dissolves with a bluish-violet colour. On pouring this solution into water, a green precipitate of emeraldine sulphate is produced.

On account of its instability, pernigraniline cannot be obtained pure in the dry state; an almost complete reversion to nigraniline occurs during drying. An attempt was therefore made to submit it without drying, to analysis by reduction, employing a paste which contained 8.45 per cent. of dry product. This was prepared as follows. Five grams of the mixture of emeraldine and nigraniline base obtained by the chlorate method were dissolved in 500 c.c. of 80 per cent. acetic acid. To the ice-cold solution was added 5 grams of ammonium persulphate dissolved in a little water, when a violet precipitate at once separated. The whole was then immediately stirred into an excess of dilute ammonia mixed with crushed ice, the temperature being kept as low as possible. After adding a little salt, the precipitate was collected, washed with several litres of water, and brought to a uniform consistency, in which the percentage of water was estimated. The following results were obtained on analysis:

| No. of experiment. | Weight of pernigraniline paste (8.45 per cent.) grams. | Vol. of TiCl_3 run in (1 litre = 0.0507 gram of hydrogen), c.c. | Vol. of TiCl_3 left unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Percentage of hydrogen on dry pernigraniline. |
|--------------------|--|--|---|---|---|
| 1 | 0.8565 | 50 | 34.7 | 0.28 | 0.949 |
| 2 | 1.1782 | 50 | 31.8 | 0.25 | 0.914 |
| 3 | 0.8900 | 50 | 36.4 | 0.29 | 0.896 |
| 4 | 1.8010 | 50 | 24.9 | 0.20 | 0.830 |

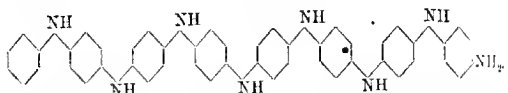
A tetraquinonoid compound of the above constitution would require for reduction to leucoemeraldine 1.11 per cent. of hydrogen. It will therefore be seen that, whilst the first titration gives a value approaching that required by this formula, there is a steady diminution in the consumption of hydrogen in the later analyses. The last titration, which was made after the paste had been kept a day, gives a hydrogen value almost corresponding with that of nigraniline (theory, 0.835 per cent.).

The above formula for pernigraniline is also supported by the figures given on p. 2396 for the consumption of chromic acid required to oxidise emeraldine and nigraniline to pernigranilino chromate. Thus, calculating the whole chromic acid as oxygen, the results are:

| | Oxygen consumed, per cent. | $\text{C}_{26}\text{H}_{34}\text{N}_2 + \frac{1}{2}\text{CrO}_3$ requires, per cent. |
|----------------------|----------------------------|--|
| From emeraldine..... | 6.13 | 5.95 |
| „ nigraniline | 3.98 | 3.79 |

It will be seen that the above formula for pernigraniline is the same as that assigned by Willstätter and Dorogi to the preparations which they call "tetraquinonoid aniline-black." The great instability of pernigraniline is, however, entirely inconsistent with the assumption that these products are identical, since the treatment to which Willstätter and Dorogi's preparations were subjected would have completely decomposed pernigraniline, and even the drying alone, without treatment with acid, would have converted it into nigraniline.

Leucoemeraldine.



This product is readily prepared by reducing either emeraldine or nigraniline with a strong reducing agent. For instance, the mixture of emeraldine and nigraniline bases obtained by the chlorate oxidation was moistened with alcohol in a mortar, and then ground to a paste with a concentrated solution of sodium hyposulphite and a little ammonia. The precipitate was collected, washed, and dried in a vacuum.

A better method consists in moistening the dry base with pure dry ether, and grinding the paste with an equal weight of phenylhydrazine. It is then thrown on a filter, and washed with dry ether until the excess of phenylhydrazine is removed, after which the product is dried quickly on a porous plate.

Leucoemeraldine forms a pale brown, amorphous powder, probably colourless when pure, which does not melt below 350°. It is fairly stable when dry, but when exposed to air in a damp state it becomes blue. It is insoluble in most solvents, but dissolves to a slight extent in pyridine. In 80 per cent. acetic acid or in 60 per cent. formic acid, it is sparingly soluble.

The constitution assigned to leucoemeraldine above is supported by the fact that four atoms of hydrogen are required for its formation from emeraldine, and six atoms for its formation from nigraniline.

Willstätter and Dorogi's Blacks.

In order to ascertain how far the products examined by these authors, and termed "triquinonoid aniline-black" and "tetraquinonoid aniline-black," compare in properties with the foregoing compounds, we have prepared them by following exactly the prescriptions given. The properties of the products we obtained are given in the following table:

| Product. | 80 per cent. acetic acid. | 60 Per cent. formic acid. | Pyridine. |
|---|---|--|---|
| Persulphate Black. (W. & D.) | Considerable portion soluble with bright bluish-green colour. | Partly soluble with bright green colour. | Considerable portion soluble with deep blue colour. |
| Bichromate Black. (W. & D.) | As above. | As above. | As above. |
| Chlorate Black : triquinonoid, 6 hours. (W. & D.) | Small part soluble with dull greenish colour. | Nearly insoluble. | Trace only soluble with pale blue colour. |
| Chlorate Black : triquinonoid, 23 hours. (W. & D.) | Trace soluble with dull greenish colour. | Insoluble. | Very sparingly soluble with pale blue colour. |
| Chlorate Black : tetraquinonoid, 6 hours. (W. & D.) | Small part soluble with dull greenish colour. | Insoluble. | As above. |
| Chlorate Black : tetraquinonoid, 22 hours. (W. & D.) | Sparingly soluble with greenish colour. | Very sparingly soluble. | As above. |

It will thus be seen that these products differ entirely from the emeraldine, nigraniline, and permigraniline described above. They appear to be mixtures containing emeraldine, together with further condensation products. Three of them were submitted to successive extractions with cold 80 per cent. acetic acid until nothing further dissolved. The following were the results obtained:

| | Persulphate Black (W. & D.), per cent. | Bichromate Black (W. & D.), per cent. | Chlorate Black : triquinonoid (W. & D.), per cent. |
|-----------------------|--|---|---|
| Soluble portion | 51.5 | 60.0 | 80.0 |
| Insoluble portion ... | 48.5 | 40.0 | 20.0 |

Oxidation of o-Toluidine.

It has long been known to technologists that *o*-toluidine, when oxidised on the fibre, gives rise to a black which is not so brilliant as aniline-black, but which has less tendency to "green." No attempt has apparently been made to prepare this dye or its intermediate compounds in substance.

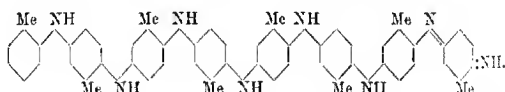
We have found that under the same conditions as employed for aniline the oxidation proceeds in an analogous manner, giving corresponding products. It appears, however, that the primary oxidation products are rather less stable than in the aniline series,

being more prone to undergo polymerisation, and that the higher quinonoid products are less easily formed, and more readily revert to the lower. The best results were obtained by conducting the oxidation without any excess of mineral acid. Thus, 33 grams of *o*-toluidine and 34 grams of hydrochloric acid (33 per cent.) were dissolved in 700 c.c. of water, with the addition of 16.8 grams of sodium chlorate and 2 drops of syrupy vanadium chloride. After being kept for three days at the ordinary temperature, the greenish-blue precipitate was collected, washed with water, basified with ammonia, and then repeatedly extracted with 90 per cent. alcohol in order to remove a soluble by-product (? homologue of Willstätter's blue imide). It was then dried at 30–35°. The product is a violet-blue powder of indigo-like appearance. It is insoluble in most solvents, but dissolves readily in pyridine with a blue colour, and in 80 per cent. acetic acid or 60 per cent. formic acid with a dull yellowish-green colour. It contains 4.6 per cent. of water and 2.0 per cent. of chlorine.

The analysis by reduction was effected in the same manner as employed for emeraldine.

| No. of experiment. | Vol. of TiCl_3 run in, c.c. | Vol. of TiCl_3 unoxidised, c.c. | Vol. of TiCl_3 oxidised by air, c.c. | Hydrogen value of 1 litre TiCl_3 , gram. | Percentage on pure dry substance. |
|--------------------|--------------------------------------|--|---|---|-----------------------------------|
| 1 | 50 | 45.43 | 0.36 | 0.0506 | 0.228 |
| 2 | 50 | 45.15 | 0.36 | 0.0506 | 0.243 |
| 3 | 50 | 44.71 | 0.36 | 0.0506 | 0.267 |
| 4 | 50 | 44.89 | 0.36 | 0.0506 | 0.267 |
| 5 | 50 | 45.88 | 0.37 | 0.0506 | 0.263 |
| 6 | 50 | 45.25 | 0.36 | 0.0506 | 0.238 |
| Mean..... | | | | | 0.239 |

A monoquinonoid compound of the constitution:



would require 0.24 per cent. of hydrogen for reduction to the leuco-compound. It therefore appears that the product of the oxidation of *o*-toluidine is the protoemeraldine of this series.

Another preparation in which an excess of acid was used in the oxidation gave as the average consumption of hydrogen for reduction 0.360 per cent. This preparation was therefore apparently a mixture of the tolu-protoemeraldine with tolu-emeraldine.

Attempts to oxidise tolu-protoemeraldine into a higher oxidation stage by means of hydrogen peroxide and ammonia, employing the same conditions as those used for nigraniline, gave a negative result. The product still dissolved in acetic acid with a green colour, and

afforded the same reduction figures as before. On the other hand, on addition of chromic acid or persulphate to the acetic acid solution, the colour first becomes blue and then violet, as in the aniline series. It therefore appears that the formation of the tolu-nigraniline does not take place with the same facility as with the lower homologue, a conclusion which is supported by the fact that no tolu-nigraniline was ever produced in our experiments with the chlorate and vanadium oxidation.

Oxidation of Other Amines.

The oxidation of various primary amines was studied under the same conditions as employed in the preparation of emeraldine. *o*-Chloroaniline gave emeraldine-like products; *m*-chloroaniline gave none. *o*-Anisidine underwent oxidation in a different direction, apparently through elimination of the methyl groups. Dimethylaniline remained unattacked.

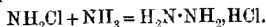
Conclusions.

1. There are four quinonoid stages derived from the parent compound leucoemeraldine.
2. The minimum molecular weights of these primary oxidation products of aniline are in accordance with an eight-nuclear structure.
3. The conversion of emeraldine into nigraniline consumes one atom of oxygen.
4. The conversion of emeraldine into pernigraniline consumes two atoms of oxygen.
5. The conversion of nigraniline into pernigraniline consumes one atom of oxygen.
6. The reduction of emeraldine to leucoemeraldine consumes four atoms of hydrogen.
7. The reduction of nigraniline to leucoemeraldine consumes six atoms of hydrogen.
8. The reduction of pernigraniline to leucoemeraldine consumes eight atoms of hydrogen.
9. The reduction of tolu-protoemeraldine consumes two atoms of hydrogen.
10. None of these products are properly entitled to be considered as aniline-black, but are intermediate products in the formation of the latter.

CCXLIV.—*Chloroamine Reactions. Methylene-chloroamine.**

By CHARLES FREDERICK CROSS, EDWARD JOHN BEVAN, and
WILLIAM BACON.

CHLOROAMINE, NH_2Cl , although not yet isolated, has been closely characterised by its reactions in solution. Raschig (*Ber.*, 1907, 40, 4586) has verified the above formula by the synthesis of hydrazine according to the equation:

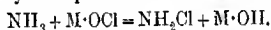


In oxidising actions, the chloroamine chlorine reacts as the chlorine of hypochlorites, thus:



from which, and in view of its formation by interaction of hypochlorites and ammonium salts, it might be formulated as NH_2OCl .

From a general view of its oxidising reactions, however, these are found in many and typical cases to be sharply differentiated from those of the hypochlorites, and hence its formation from hypochlorites is rather represented by the equation:



It may be inferred from Raschig's investigations that such reactions would be a general characteristic of amino compounds, and we have studied certain of these in relation to their conversion into chloroamines.

As a result, we have been able to characterise the compounds obtained from proteins by the action of chlorine as chloroamines (Cross, Bevan, and Briggs, *J. Soc. Chem. Ind.*, 1908, 27, 260).

Such compounds have been known since 1840 (Mulder, *Berzelius Jahresber.*, 19, 734), and their formation has been made the basis of quantitative analytical methods (Rideal and Stewart, *Analyst*, 1897, 22, 228), depending on the separation of these derivatives, which are insoluble in water, followed by nitrogen estimations in the precipitated compounds. These methods we find are much simplified by estimations of chloroamine chlorine according to the well-known chlorimetric methods.

We have described such methods in detail as applicable to the estimation of gelatin, and we have also applied similar reactions to the elucidation of industrial processes which are attended by the formation of chloroamines, notably the bleaching of flax textiles (*loc. cit.*).

In the case of gelatin it is noteworthy that the chloroamine

* This name is retained pending the final settlement of the constitution of the compound, in order to indicate its relation to chloroamine.

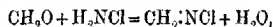
lative is of constant composition, the chloroamine chlorine ($=\text{Cl}_2$) representing 18.3 per cent. of original gelatin, and after dehydration is stable in the air.

Methylenechloroamine.

The typical reactions of chloroamine, especially with aromatic amines and phenols, have further been elucidated by Raschig (*Chem. Zeit.*, 1907, 31, 126; *Zeitsch. angew. Chem.*, 1907, 20, 2065).

In extending these investigations, we have observed a reaction of special interest which we will briefly describe, as it involves a new chloroamine, readily obtainable in crystalline form.

Formaldehyde and chloroamine in aqueous solution react according to the equation:



the resulting methylenechloroamine separates in well-formed crystals, and on recrystallisation from chloroform, in which it is easily soluble, it is obtained in needles of 10 to 15 mm. in length. To prepare this compound, approximately semi-normal solutions of hypochlorites ($\text{Cl} = 1.8$ grams per 100 c.c.) are treated with ammonium chloride, and formaldehyde solution added in the cold. The proportions are taken somewhat in excess of the calculated. On keeping at, or under, 15° , the solution becomes milky, and the compound then crystallises. It is obtained as a mass of brilliant, felted needles. The yields under these conditions are 30 to 40 per cent. of the calculated.

For analysis, the substance is dissolved in chloroform, the solution being left for some hours in contact with calcium chloride, and poured off through a dry filter, when, after some time, the substance crystallises out.

Many preparations have been analysed, and the numbers are in close accordance with the formula $\text{CH}_2\text{:NCl}$.

The following results are typical:

Total chlorine, by digestion with sodium sulphite and precipitation as silver chloride:

0.1255 gave 0.2815 AgCl.

"Active chlorine," by digestion with potassium iodide solution and titration of the liberated iodine:

0.3124 liberated $\text{I} = 99.8$ c.c. $N/10$ -thiosulphate.

Nitrogen, by digestion with ferrous sulphate, in presence of sulphurous acid, and distillation from alkalis; the nitrogen being obtained as ammonia:

0.1135 gave $\text{NH}_3 = 18.2$ c.c. $N/10$ -HCl.

Found, Total $\text{Cl} = 55.4$; "Active" $\text{Cl} = 56.7 \times 2$; $\text{N} = 22.4$.

$\text{CH}_2\text{:NCl}$ requires Total $\text{Cl} = 55.9$; "Active" $\text{Cl} = 55.9 \times 2$;
 $\text{N} = 22.05$ per cent.

Molecular-weight determinations even by cryoscopic methods present difficulties, due to the instability and reactivity of the compound, but the following numbers calculated from the depression of the freezing point of benzene were obtained:

Found, M.W. = 133.0, 132.7, 131.7.

$2\text{CH}_2\text{NCl}$ requires M.W. = 127.

Our incidental observations indicate a change of solubility in benzene from 2.7 to 1.5 per 100 c.c. at 5° , and polymerisation probably has to be taken into account. This point will be resolved by further investigation.

Methylen-chloramine is soluble in 20 to 30 parts of ether at the ordinary temperature, and similarly in benzene, as indicated above; it is only sparingly soluble in paraffinoid hydrocarbons.

It decomposes spontaneously in ordinary air, and when heated at $50-60^\circ$ it decomposes explosively, leaving a residue of ammonium chloride.

As shown by the analytical results, it may be quantitatively hydrolysed and reduced, ammonia and formaldehyde being regenerated, and by certain decompositions it yields hydrocyanic acid as a main product.

The investigation is being continued.

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LONDON, W.C.

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ERRATA.

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| Page. | Line | |
|-------|------|---|
| 2274 | 16 | for "3-Methyl." read "2-Methyl." |
| 2274 | 15 | .. " $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHMe} \\ \text{CO} \end{smallmatrix} \text{CH}(\text{CO}_2\text{Et})$ " read $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{CMe}(\text{CO}_2\text{Et})$ |
| 2275 | 1 | "3-methyl." read "2-methyl." |
| 2275 | 10 | .. "3-Methyl." .. "2-Methyl." |
| 2275 | 10 | .. " $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHMe} \\ \text{CO} \end{smallmatrix} \text{CH}_2$ " read " $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{CHMe}$." |
| 2275 | 11 | .. "3-methyl." read "2-methyl." |

* From bottom.

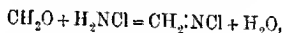
derivative is of constant composition, the chloroamine chlorine ($=\text{Cl}_2$) representing 18.3 per cent. of original gelatin, and after dehydration is stable in the air.

Methylenechloroamine.

The typical reactions of chloroamine, especially with aromatic amines and phenols, have further been elucidated by Raschig (*Chem. Zeit.*, 1907, 31, 126; *Zeitsch. angew. Chem.*, 1907, 20, 2065).

In extending these investigations, we have observed a reaction of special interest which we will briefly describe, as it involves a new chloroamine, readily obtainable in crystalline form.

Formaldehyde and chloroamine in aqueous solution react according to the equation:



the resulting methylenechloroamine separates in well-formed crystals, and on recrystallisation from chloroform, in which it is easily soluble, it is obtained in needles of 10 to 15 mm. in length. To prepare this compound, approximately semi-normal solutions of hypochlorites ($\text{Cl} = 1.8$ grams per 100 c.c.) are treated with ammonium chloride, and formaldehyde solution added in the cold. The proportions are taken somewhat in excess of the calculated. On keeping at, or under, 15° , the solution becomes milky, and the compound then crystallises. It is obtained as a mass of brilliant, felted needles. The yields under these conditions are 30 to 40 per cent. of the calculated.

For analysis, the substance is dissolved in chloroform, the solution being left for some hours in contact with calcium chloride, and poured off through a dry filter, when, after some time, the substance crystallises out.

Many preparations have been analysed, and the numbers are in close accordance with the formula CH_2NCl .

The following results are typical:

Total chlorine, by digestion with sodium sulphite and precipitation as silver chloride:

0.1235 gave 0.2815 AgCl.

"Active chlorine," by digestion with potassium iodide solution and titration of the liberated iodine:

0.3121 liberated $\text{I} = 99.8$ c.c. $N/10$ thiosulphate.

Nitrogen, by digestion with ferrous sulphate, in presence of sulphurous acid, and distillation from alkalis; the nitrogen being obtained as ammonia:

0.1135 gave $\text{NH}_3 = 18.2$ c.c. $N/10\text{-HCl}$.

Found, Total $\text{Cl} = 55.4$; "Active" $\text{Cl} = 56.7 \times 2$; $\text{N} = 22.4$.

CH_2NCl requires Total $\text{Cl} = 55.9$; "Active" $\text{Cl} = 55.9 \times 2$;
 $\text{N} = 22.05$ per cent.

Molecular-weight determinations even by cryoscopic methods present difficulties, due to the instability and reactivity of the compound, but the following numbers calculated from the depression of the freezing point of benzene were obtained:

Found, M.W. = 133.0, 132.7, 131.7.

$2\text{CH}_2\text{NCl}$ requires M.W. = 127.

Our incidental observations indicate a change of solubility in benzene from 2.7 to 1.5 per 100 c.c. at 5° , and polymerisation probably has to be taken into account. This point will be resolved by further investigation.

Methylenechloramine is soluble in 20 to 30 parts of ether at the ordinary temperature, and similarly in benzene, as indicated above; it is only sparingly soluble in paraffinoid hydrocarbons.

It decomposes spontaneously in ordinary air, and when heated at 50 – 60° it decomposes explosively, leaving a residue of ammonium chloride.

As shown by the analytical results, it may be quantitatively hydrolysed and reduced, ammonia and formaldehyde being regenerated, and by certain decompositions it yields hydrocyanic acid as a main product. The investigation is being continued.

4, NEW COURT,
LONDON, W.C.

CCXLV.—*Narcissine: an Alkaloid from the Bulb of the Common Daffodil (Narcissus pseudonarcissus).*

By ARTHUR JAMES EWINS.

IN 1878 a paper was published by Ringer and Morshead (*J. Physiol.* 1, 437), entitled "On the physiological action of narcissia, an alkaloid obtained from the bulb of the common daffodil (*Narcissus pseudonarcissus*).” This work contained a detailed account of experiments carried out on men and frogs with an alkaloid or with extracts containing the alkaloid, which had been obtained by Gerrard from the bulb of the common daffodil. From experiments carried out with extracts obtained from bulbs in the resting stage and from bulbs of the flowering plants, the authors concluded that the action of the alkaloid present in the extracts from the resting bulbs was similar to that of pilocarpine, whereas that present in the extracts from the bulbs of the flowering plants closely resembled atropine in action. The alkaloid obtained by Gerrard from both extracts nevertheless appeared to be the same in general chemical properties.

In view of these statements and of the fact that no reference to "narcissia" or to any alkaloid obtained from the bulbs of the daffodil can be found in chemical literature, it appeared to be of interest to obtain the alkaloid in a pure state, in order that a more detailed investigation of its chemical and physiological properties might be made, more especially as the alkaloids which have been obtained from monocotyledons are comparatively few in number.

The bulbs of a cultivated variety of the daffodil (*Narcissus pinnipetals*), being more readily obtainable than the variety mentioned above, were first employed in the investigation. From these bulbs, however, the extracts obtained from the resting or flowering bulbs gave only traces of alkaloidal reactions, and the isolation of the alkaloid was obviously hopeless. With the bulbs of the wild daffodil (*Narcissus pseudonarcissus*), much more satisfactory results were obtained. From these a crystalline alkaloid was readily obtained. From the resting bulbs a yield of approximately 0.2 per cent. of the dried material, and from the flowering bulbs only about 0.1 per cent., was obtained. The alkaloid, which, in accordance with modern usage, it is suggested he called "narcissine," rather than "narcissia," was the same in both cases.

Narcissine has been found by analyses and molecular-weight determination to possess the formula $C_{16}H_{17}O_3N$. The alkaloid is characterised by very great stability, and on that account and owing to the small amount of material available (about 3 grams only), no light has been thrown on its probable constitution. The nitrogen present is tertiary, since nitrous acid is without action on the alkaloid, and treatment with methyl iodide produced an amorphous product which was probably the methiodide of the base, but which could not be crystallised for analysis. The action of hydriodic acid (Zeisel) showed the absence of methoxy-groups, but on very strongly heating, a very small amount of methyl iodide was evolved, and the residue on suitable treatment yielded a solution which gave a violet coloration with ferric chloride, the phenolic substance being extracted from its acid solution by ether. The amount of substance so obtained was, however, extremely small, and further attempts to hydrolyse by means of acids yielded no crystalline product.

Fusion with potassium hydroxide yielded no better results. At temperatures up to 220° the alkaloid was only very slowly attacked, traces of alkaline vapour being evolved. Heating with the naked flame for one and a-quarter hours was required in order to decompose completely about 0.7 gram of the alkaloid. The reaction product dissolved in water gave on addition of ferric chloride a violet coloration, quickly passing to a dirty brown, with separation of a

brown, flocculent precipitate. This polyphenolic substance, again, could be extracted by ether from its acid solution, but on evaporating off the solvent only a very small quantity of a brown, amorphous product was obtained, and all attempts to obtain a crystalline product were fruitless.

On account of the relatively large number of oxygen atoms present in the molecule, it was thought possible that a carboxyl group might be present, but attempted esterification showed the absence of such grouping. For this reason and from the absence of methoxy-groups as shown by the Zeisel reaction, the formation of a polyphenolic derivative such as has been described is very possibly due to the presence in the molecule of a methylenedioxy-grouping and a phenolic bridge oxygen. The stability of the alkaloid would seem to support such a view, although there is, of course, no direct evidence of such structure.

Experiments with regard to the physiological action of the alkaloid were carried out in these laboratories by Dr. P. P. Laidlaw, to whom I am indebted for the following account of its action. As tested on frogs and cats, the alkaloid showed no action in any way similar to that of pilocarpine or of atropine. 0.125 Gram, given by mouth to a cat, caused nausea, vomiting, salivation, and purgation. The salivation was not, however, similar to that produced by pilocarpine, since it could not be produced on the anaesthetised animal.

EXPERIMENTAL.

Preparation of the Alkaloid.

Two thousand five hundred bulbs of the common daffodil (*Narcissus pseudonarcissus*), weighing approximately 4 kilos., were dried at a temperature of about 40°. The weight of the dried product was 1400 grams. The substance was finely ground and extracted for about six hours with hot alcohol (97 per cent.), and the alcoholic extract evaporated to about 200 c.c. To the dark syrupy, acid liquid was added an equal volume of water, and a very dark resinous precipitate which formed was collected. This precipitate was re-suspended in a little very dilute acid, and again collected after thoroughly shaking. The filtrate and washings were combined, and the acid liquid extracted twice with about one-third of its volume of ether. The aqueous solution was then rendered alkaline by addition of sodium carbonate, when, after some time, a precipitate formed, which consisted mainly of bunched prisms. The crystals were collected, and after recrystallisation from 90 per cent. alcohol were obtained as colourless, short, stout prisms, melting at 266—267° (bath at 250° at commencement of heating). The substance was dried first in air, then in a vacuum over sulphuric acid,

and finally at 110° , no alteration in weight taking place under these varying conditions:

0.1448 gave 0.3552 CO_2 and 0.0754 H_2O . $\text{C}=66.9$; $\text{H}=5.8$.

0.1283 „ 0.3159 CO_2 „ 0.0684 H_2O . $\text{C}=67.1$; $\text{H}=5.9$.

0.1051 „ 5.0 c.c. N_2 (moist) at 13.5° and 732 mm. $\text{N}=5.4$.

$\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C}=66.9$; $\text{H}=5.9$; $\text{N}=5.0$ per cent.

A determination of the molecular weight was made by Barger's microscopic method (Trans., 1904, **86**, 286) in glacial acetic acid. 0.060 Gram, in 1.197 grams of solvent, was intermediate between 0.19 mol. and 0.20 mol., whence $\text{M.W.}=257$. $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{M.W.}=287$.

Properties of Narcissine.—The alkaloid, as before stated, is obtained by recrystallisation from alcohol in colourless prisms, which melt at $266\text{--}267^{\circ}$ with some decomposition and formation of a red liquid. The crystals are insoluble in water or dilute sodium hydroxide, but readily soluble in dilute acid. The acid solution gives all the usual alkaloidal reactions, for example, with Meyer's reagent, with a solution of iodine in potassium iodide, and with phosphotungstic acid. The crystalline product is only very sparingly soluble in methyl alcohol, ethyl alcohol, ethyl acetate, or acetone, moderately so in pyridine, nitrobenzene, or glacial acetic acid, and insoluble in ether or chloroform. A determination of its solubility in absolute ethyl alcohol showed that one part by weight of the alkaloid was soluble in 284 parts of boiling alcohol and in 340 parts of alcohol at 15° .

The alkaloid is laevorotatory. 0.166 Gram, made up to 100 c.c. with absolute alcohol, gave, in a 2.2-dem. tube at 10° , $\alpha_D -0.35^{\circ}$, whence $[\alpha]_D^{20} = -95.8^{\circ}$.

The alkaloid dissolves in concentrated sulphuric acid, producing a deep red solution, which slowly becomes reddish-brown on keeping.

Narcissine Hydrochloride, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N} \cdot \text{HCl}$.—0.3 Gram of crude narcissine was dissolved in dilute hydrochloric acid, and the solution evaporated to dryness over potassium hydroxide in a desiccator. The resulting crystalline product was dissolved in hot 90 per cent. alcohol, and after treatment with a little blood-charcoal, the solution, on cooling, deposited the hydrochloride in long, thin prisms, melting at $198\text{--}199^{\circ}$. Yield, 0.27 gram:

0.2737 gave 0.1176 AgCl . $\text{Cl}=10.6$.

$\text{C}_{16}\text{H}_{17}\text{O}_4\text{N} \cdot \text{HCl}$ requires $\text{Cl}=10.9$ per cent.

CCXLVI.—*The Action of Halogens on Mercuricamphor Compounds.*

By JAMES ERNEST MARSH.

THE work described in this paper is a continuation of that published by Mr. Struthers and the author on the mercury derivatives of camphor (*Trans.*, 1909, **95**, 1777).

In the former paper it was shown that di-iodocamphor was obtained by the action of iodine on one of the mercury derivatives. It is now found that the same di-iodocamphor is formed from the three mercury compounds, namely, those which have the formulae: $C_{10}H_{14}OHg_2I_2$, $(C_{10}H_{11}O)_2Hg_4I_2$, and $(C_{10}H_{11}O)_4Hg_5I_2$. The method of preparation is the same in each case. The mercury compound is treated with an aqueous solution of iodine and potassium iodide, enough iodine being taken to combine with the mercury and the camphor residue, and enough potassium iodide to hold the mercuric iodide in solution. The product of the reaction is extracted with chloroform, and the chloroform solution washed with sodium hydroxide, dried, and rapidly evaporated. The di-iodocamphor is then left in the crystalline form, and, after washing with light petroleum, is practically pure. A small amount of camphorquinone, which is formed, is removed by the petroleum. If the operation is carried out carefully, the yield is nearly quantitative, but if the substance is left too long in the chloroform solution the amount obtained is less satisfactory, as it decomposes in solution. Even when the substance is partly decomposed by being overheated or left too long in solution, a good product can still be obtained by boiling with sodium hydroxide solution, and washing the residue with petroleum. Di-iodocamphor, when in solution, rapidly decomposes with separation of iodine. In order to recrystallise it, the best solvent was found to be aqueous pyridine. It is very soluble in pure pyridine, and, on adding a little water, crystals at once separate. The crystals should be spread out in a thin layer to dry, as they rapidly decompose if heaped up in masses while still wet with the solvent. The compound decomposes a little above its melting point, 108° , with evolution of iodine. It is stable in presence of alkalis, and may be kept under a solution of sodium hydroxide. It may be boiled with aqueous sodium hydroxide without decomposition, and it is not appreciably volatile in steam.

Action of Oxygen on Di-iodocamphor. Camphorquinone.

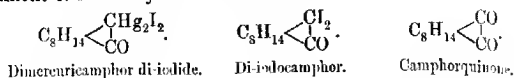
Although in the crystalline form, di-iodocamphor is stable when exposed to air, when dissolved in chloroform it decomposes with separation of iodine. One atom of oxygen takes the place of the two atoms of iodine, and camphorquinone is formed, along with a small quantity of camphoric anhydride.

To obtain camphorquinone in this way, air dried by sulphuric acid is bubbled through a solution of di-iodocamphor in chloroform. Iodine at once begins to separate, as is shown by the change in the colour of the solution. Fresh chloroform is added, when necessary, to make good the loss by evaporation. When the action is finished, the product is mixed with a solution of sodium hydroxide and distilled in a current of steam. The alkali serves not only to combine with the free iodine, but also to convert the camphoric anhydride into sodium camphorate; otherwise the anhydride distils over in the steam, and renders the quinone impure. The quinone appears in the distillate as yellow crystals, and also colours the water yellow. It is extracted with ether or, better, with chloroform. The ethereal extract gave, on evaporation, crystals melting at 196—197°, which, after recrystallisation from alcohol, melted at 198—199°. (Found, C=71.7; H=8.4. Calc., C=72.3; H=8.4 per cent.)

The yield of camphorquinone by this method is more than 90 per cent. of that required by theory. This method should serve for the production of camphorquinone in any quantity from camphor, since the yield of the mercury compound from camphor and that of di-iodocamphor from the mercury compound are both nearly quantitative. Further, all the mercury and iodine employed in the reactions can be recovered in the form of mercuric iodide, and used again for the preparation of the camphor-mercury compound.

Camphorquinone is readily oxidised to camphoric acid by warming with a solution of sodium peroxide; the crystals dissolve, and the yellow colour of the solution disappears; on acidifying, camphoric acid, melting at 186°, separates. It is converted by the action of acetyl chloride into camphoric anhydride, melting at 220°. This conversion of di-iodocamphor into camphorquinone and camphoric acid shows that the iodine has replaced the hydrogen in the CH₂ group, which is adjacent to the CO group. It also shows further that, in the mercury derivatives, the Hg^{II} and (HgI) groups are similarly situated in the $\alpha\alpha'$ position. This was anticipated by Mr. Struthers and myself from the circumstance that the only ketones which we found to give mercury derivatives were those having hydrogen in the α -position. The structural

relationship of the mercury and iodine derivatives to camphor. quinuone is shown by the formulae:



Action of Bromine on the Mercuricamphor Compounds.
αα'-Dibromocamphor.

The action of bromine on the mercuricamphor compounds is not so simple as is the action of iodine. In the main, the reaction proceeds with the production of αα'-dibromocamphor, melting at 61°. The action is, however, complicated by liberation of iodine and its action, also by the oxidising action of the bromine, and further by the action of the hydrogen bromide produced in the oxidation.

To prepare αα'-dibromocamphor, the mercury compound $(\text{C}_{10}\text{H}_{14}\text{O})_4\text{Hg}_3\text{I}_2$ is preferably employed, since it contains less iodine than the other mercuricamphor compounds.

The mercuricamphor compound is mixed with half its weight of powdered mercuric oxide, and this mixture is added gradually to a solution in water of the requisite amounts of bromine and potassium bromide, so that the whole of the mercuric bromide formed is dissolved in the water. The mixture is stirred all the time with a turbine, and it becomes warm as the reaction proceeds. When cold, the mixture is extracted with chloroform. The chloroform solution is washed with sodium hydroxide and water, dried, and evaporated. The crude dibromocamphor left on evaporation is purified by solution in light petroleum. The petroleum solution is filtered, if necessary, from a small quantity of a crystalline substance, which is referred to later. On evaporation of the petroleum, the residue is distilled under diminished pressure. αα'-Dibromocamphor distils at about 175°/20 mm., and solidifies in the receiver. After recrystallisation from alcohol, it melted at 61°. (Found, Br=51.5. Calc., Br=51.6 per cent.)

Mr. T. V. Barker examined the crystals with the goniometer, and found the measurements to be identical with those given by Zepharowich for αα'-dibromocamphor.

By its production in this way, the dibromocamphor is brought into relationship with di-iodocamphor, camphorquinone, and camphoric acid; hence its constitution as an αα'-compound is confirmed.

The same dibromocamphor is produced by the action of bromine in chloroform instead of aqueous solution. It is also obtained from the mercury compound $\text{C}_{10}\text{H}_{14}\text{OHg}_2\text{I}_2$, and by the action of bromine on di-iodocamphor in chloroform solution. It may be presumed

to be also obtainable, like di-iodocamphor, from the intermediate mercury compound $(C_{10}H_{14}O)_3Hg_4I_2$.

The use of mercuric oxide in the preparation of dibromocamphor needs some explanation. It was found to prevent the formation of by-products. It probably acts by combining with any hydrogen bromide which may be formed, and thus preventing the decomposition of the mercuriccamphor compound into camphor and mercuric bromide.

The crystalline compound insoluble in petroleum is obtained when mercuric oxide is not employed in the reaction; and at the same time some α -monobromocamphor is formed. The former substance crystallised well from alcohol, and melted at 159° . Numerous analyses were made of this substance, prepared under varying conditions. The analyses do not indicate the presence of a single substance, but of a mixture intermediate between the compounds $C_{10}H_{14}O_2Br_2$ and $C_{10}H_{14}O_2I_2$, with no simple relation between the bromine and the iodine atoms. When bromine acts on di-iodocamphor, a similar substance is formed with relatively more iodine and less bromine in its composition, and of a higher melting point, namely, 172° . A product of a similar nature is obtained with chlorine taking the place of bromine, when a chloroform solution of di-iodocamphor is acted on by chlorine.

When the mercuriccamphor compound is treated with iodine bromide, IBr, or by iodine chloride, ICl, the principal product in each case is di-iodocamphor.

I wish to thank my assistant, Mr. F. Hall, for his excellent help in this investigation.

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OXFORD.

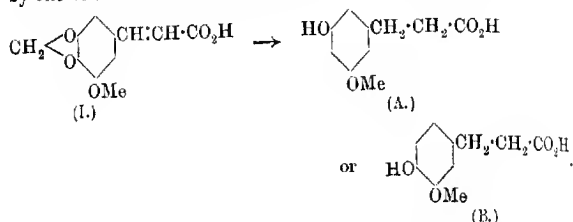
CCXLVII.—*Action of Sodium Amalgam on Methylene Ethers.*

By ARTHUR HENRY SALWAY.

IN the course of the author's previous investigations, which led to the synthesis of cotarnine (Trans., 1909, **95**, 1204; this vol., 1208), the reduction of 3-methoxy-4:5-methylenedioxy-cinnamic acid (I) was described. In this reaction it was observed that the normal reduction product, namely, β -3-methoxy-4:5-methylenedioxyphenylpropionic acid (II), was invariably accompanied by a considerable proportion of a by-product. This substance, of which

no account was given in the previous communications, has now been isolated in sufficient quantity to render its complete examination possible.

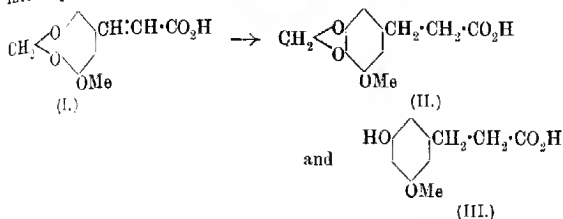
The purified compound was found to possess the properties of a phenol and of a carboxylic acid, and gave analyses corresponding with the empirical formula $C_{10}H_{12}O_4$. It is evident that the production of such a compound from 3-methoxy-4:5-methylenedioxy-cinnamic acid (I) can only be explained by the simultaneous reduction of the aliphatic side-chain and the substitution of a hydroxyl group for the methylenedioxy-complex. The constitution of the resulting compound would therefore appear to be represented by one of the two formulæ A and B:



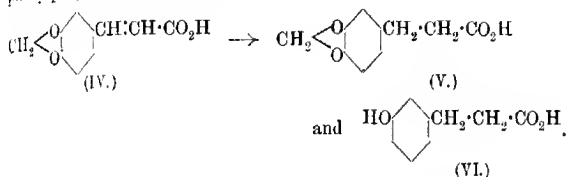
In order to decide between these formulæ, the substance was converted by means of methyl sulphate into a dimethoxyphenylpropionic acid, which melted at 61–62°. The dimethoxy-acid corresponding with B, namely, β -3:4-dimethoxyphenylpropionic acid, melts, according to Tiemann and Nagai (*Ber.*, 1878, 11, 653), at 97°, whilst the 3:5-dimethoxy-acid corresponding with A does not appear to have been hitherto described. Formula B is thus shown to be inadmissible, and consequently A most probably represents the constitution of the substance under examination. Positive evidence in support of this conclusion was obtained by converting the dimethoxypropionic acid into the corresponding dimethoxybenzoic acid by oxidation with alkaline permanganate solution. The product of oxidation melted at 180–181°, and was found to be identical with 3:5-dimethoxybenzoic acid. It is thus shown that in the reduction of 3-methoxy-4:5-methylenedioxy-cinnamic acid (I), the normal reaction is accompanied by a secondary change involving the disruption of the methylenedioxy-complex and the formation of β -5-hydroxy-3-methoxyphenylpropionic acid (II), according to the scheme on p. 2415.

It was next deemed of interest to ascertain whether other methylene ethers are capable of undergoing a similar change, and accordingly piperonylacrylic acid (IV) was subjected to the action of sodium amalgam. In this case, also, it was found that reduction

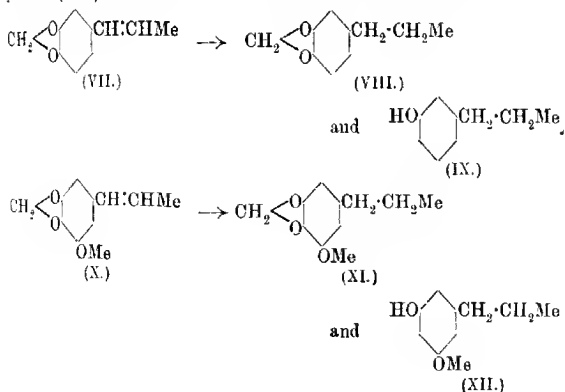
takes place with partial conversion of the methylenedioxy-complex into a hydroxyl group, the products of the reaction being a mixture



of β :3:4-methylenedioxyphenylpropionic acid (V) and β :3-hydroxy-phenylpropionic acid (VI):



A similar reaction has been observed by Ciamician and Silber (*Ber.*, 1890, **23**, 1162), who have shown that *isosafrole* (VII), when reduced by sodium and alcohol, is converted into a mixture of 3:4-methylenedioxypropylbenzene (VIII) and *m*-propylphenol (IX), whilst Thoms (*Ber.*, 1903, **36**, 3449) records the fact that *isomyristicin* (X), under similar conditions, yields both 5-methoxy-3:4-methylenedioxypropylbenzene (XI) and 5-methoxy-3-propylphenol (XII):



It is worthy of note that in each of the above examples of the displacement of a methylenedioxy-complex by a hydroxyl group, the latter appears in the meta-position with regard to the side-chain. Moreover, the position of the unsaturated linking in the side-chain is of importance in determining the course of the reaction, since only those compounds which contain the unsaturated linking in the $\alpha\beta$ -position with regard to the benzene nucleus appear to be capable of undergoing the above-described transformation. Thus, for example, the methylenedioxy-group of *isomyristicin* (X) is readily decomposed by means of sodium and alcohol, whilst *myristicin*, in which the unsaturated linking is in the $\beta\gamma$ -position, does not suffer this change.

EXPERIMENTAL.

Reduction of 3-Methoxy-4:5-methylenedioxybenzoic Acid (I, p. 2415).

A solution of one part of 3-methoxy-4:5-methylenedioxybenzoic acid in 20 parts of 1 per cent. aqueous sodium hydroxide was reduced by the gradual addition, with constant stirring, of 16 parts of sodium amalgam (4 per cent.). After the amalgam had been completely decomposed, the mixture was acidified, the precipitated oil extracted with ether, and the ethereal solution washed, dried, and the solvent removed. In this manner the product of reduction was obtained as a light brown oil, which gradually became crystalline. A preliminary examination of the product indicated the presence of a considerable proportion of a phenolic carboxylic acid in addition to the normal reduction product, β -3-methoxy-4:5-methylenedioxyphenylpropionic acid. In order to effect a separation of these compounds, the mixture was dissolved in alcohol and esterified by means of dry hydrogen chloride, after which the excess of alcohol was removed and the esters extracted with ether. The ethereal solution was first washed with aqueous sodium carbonate to remove any unesterified acid, and then shaken with dilute sodium hydroxide. The sodium hydroxide extract, which contained the phenolic ester, was warmed for a short time to complete the hydrolysis of the latter, then acidified and extracted with ether. This ethereal extract yielded a colourless solid, which was recrystallised from hot water, when it separated in flat, hexagonal plates, melting at 127° :

0.1103 gave 0.2482 CO_2 and 0.0635 H_2O . $\text{C} = 61.4$; $\text{H} = 6.4$.

0.2800 required for neutralisation 14.35 c.c. $N/10$ KOH.

M.W. = 195.

$\text{C}_{10}\text{H}_{12}\text{O}_4$ requires $\text{C} = 61.2$; $\text{H} = 6.1$ per cent. M.W. = 196.

As already explained in the introduction, this substance was found to be β -5-hydroxy-3-methoxyphenylpropionic acid.

β -5-Hydroxy-3-methoxyphenylpropionic acid (III, p. 2415) is readily soluble in ether, alcohol, or hot water, and crystallises from the latter in colourless, hexagonal plates, which gradually become pink on exposure to air. It is insoluble in benzene or light petroleum. Its *amide*, $\text{MeO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises from water in prismatic needles, melting at 126° .

In order to prepare the methyl derivative of the above compound, 10 grams of the phenolic acid were dissolved in methyl alcohol and 5 c.c. of methyl sulphate, and 10 c.c. of a 50 per cent. solution of potassium hydroxide added. After the vigorous reaction had subsided, the same quantities of methyl sulphate and alkali were again added, and the mixture heated for a short time on the water-bath. The alkaline liquid was then acidified and extracted with ether, when the ethereal extract yielded an oil which gradually solidified. This product was purified by crystallisation from a mixture of benzene and light petroleum, from which it separated in clusters of colourless, silky needles, melting at $61\text{--}62^\circ$:

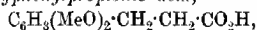
0.1076 gave 0.2490 CO_2 and 0.0649 H_2O . $\text{C}=63.1$; $\text{H}=6.7$.

0.4465 required for neutralisation 21.25 c.c. $\text{N}/10\text{-NaOH}$.

M.W.=210.

$\text{C}_{11}\text{H}_{14}\text{O}_4$ requires $\text{C}=62.9$; $\text{H}=6.7$ per cent. M.W.=210.

β -3: 5-Dimethoxyphenylpropionic acid,



is readily soluble in the usual organic solvents, excepting light petroleum. It yields an *amide*, which crystallises from a mixture of benzene and petroleum in colourless needles, melting at $80\text{--}81^\circ$. The position of the methoxy-groups in the above compound was ascertained by oxidising a quantity of the substance with a hot alkaline solution of potassium permanganate. At the end of the oxidation, the liquid was cooled, an excess of sulphur dioxide added, and the precipitated oxidation product collected. It was re-crystallised from hot water, when it separated in thin needles, melting at $180\text{--}181^\circ$. (0.2045 required for neutralisation 11.25 c.c. $\text{N}/10\text{-NaOH}$. M.W.=182. Calc., M.W.=182.)

This substance possessed all the properties of 3: 5-dimethoxybenzoic acid (Bülow and Riess, *Ber.*, 1902, **35**, 3901), and was evidently identical with that compound.

Reduction of Piperonylacrylic Acid.

The reduction of piperonylacrylic acid by means of sodium amalgam was first described by Lorenz (*Ber.*, 1880, **13**, 758), who isolated piperonylpropionic acid from the product of the reaction,

but did not record the formation of a phenolic compound. In view, however, of the results obtained in the above reduction of 3-methoxy-4:5-methylenedioxy-cinnamic acid, it seemed probable that some β -5-hydroxyphenylpropionic acid would be formed in the reduction of piperonylacrylic acid. In order to ascertain if this were the case, 20 grams of piperonylacrylic acid were reduced with sodium amalgam in the manner described in connexion with the reduction of 3-methoxy-4:5-methylenedioxy-cinnamic acid. The product was then esterified, and, by means of dilute sodium hydroxide, separated into a non-phenolic and a phenolic ester. The former amounted to 18 to 19 grams, and yielded on hydrolysis piperonylpropionic acid, melting at 85° , whilst the latter, when hydrolysed, yielded a brown oil (2 grams), which gradually solidified on agitation with benzene. This substance was purified by recrystallisation from a mixture of ether and benzene, and was thus obtained in colourless needles, melting at 110° . (0.1922 required 11.8 c.c. $N/10$ -NaOH for neutralisation. M.W. = 163. Calc., M.W. = 166.)

This compound possessed all the properties of 3-hydroxyphenylpropionic acid, and was evidently identical with it (Braunstein, *Ber.*, 1882, 15, 2050).

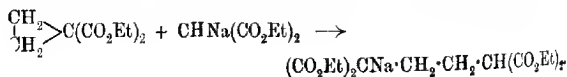
The action of sodium amalgam on piperonylacrylic acid is therefore analogous to that which takes place when 3-methoxy-4:5-methylenedioxy-cinnamic acid is reduced. The yield of phenolic acid in the latter case is, however, much greater than in the former.

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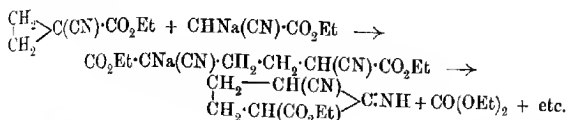
CCXLVIII.—*An Instance Illustrating the Stability of the Four-Carbon Ring.*

By ARTHUR FRED CAMPBELL and JOCELYN FIELD THORPE.

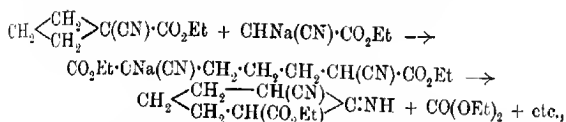
It has been shown by Bone and Perkin (*Trans.*, 1895, 67, 108) that when a derivative of *cyclopropane* which has two carbethoxy-groups attached to the same carbon atom is treated with the sodium compound of ethyl malonate, condensation ensues, with the formation of an open-chain ethyl ester in the following way:



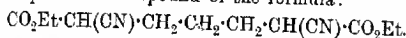
This reaction has been made use of by us for the preparation of certain open-chain nitriles (Trans., 1909, 95, 697; this vol., 1002), which we found possessed the property of readily passing into imino-derivatives of *cyclopentane* when treated with sodium ethoxide, thus:



Wishing to prepare the open-chain compound containing one more methylene group, in order to study the conditions under which it passed into a derivative of *cyclohexane*, we decided to apply the above reaction to ethyl 1-cyanocyclobutane-1-carboxylate, in the hope that the following reaction would ensue:

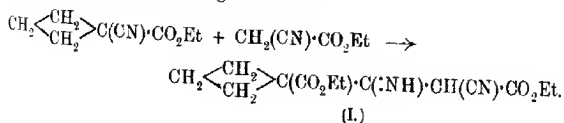


and that in this way an imino-derivative of *cyclohexane* would be formed. We found that this condensation yielded considerable quantities of a crystalline substance melting at 111°, which possessed the molecular formula $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_2$, that is to say, it seemed to be the normal open-chain compound of the formula:

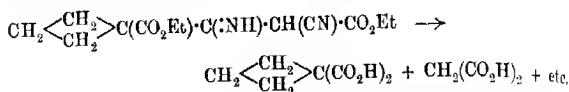


All attempts, however, to induce it to react with sodium ethoxide proved unavailing, and we consequently decided that the imino-derivatives of the six-membered ring could not be produced in the same manner as those of *cyclopentane*.

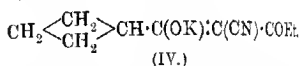
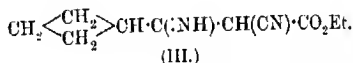
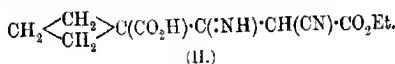
Before recording this fact, we subjected the open-chain compound to complete hydrolysis in order to prove its constitution by the formation of pimelic acid, when it was found that instead of this acid the product consisted of *cyclobutane-1:1*-dicarboxylic acid and malonic acid. Subsequent experiments showed conclusively that the condensation product of the formula $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_2$ was *ethyl β-imino-α-gano-1-carbethoxy-β-cyclobutyl-1-propionate* (I), and that it had been formed in the following manner:



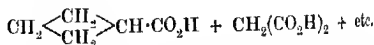
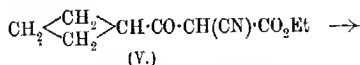
The hydrolysis had evidently therefore taken place in accordance with the equation:



The constitution of the imino-compound was further shown by the products formed from it on partial hydrolysis. Thus, with dilute alkali hydroxide, it yields the alkali salt of *ethyl β-imino-α-cyano-1-carboxy-β-cyclobutyl-1-propionate*, from which the free ethyl hydrogen salt (II) can be prepared by the action of acids. This substance exists in two well-defined modifications, which melt at 75° and 156° respectively. We have named these compounds the α- and β-forms of the ethyl hydrogen salt, as we have been unable to determine their structural relationship:



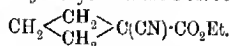
Both modifications lose carbon dioxide when heated, and pass into *ethyl β-imino-α-cyano-β-cyclobutylpropionate* (III), a tautomeric amino-imino-compound, which, when treated with potassium hydroxide, passes into the stable *potassium* salt (IV). When a solution of this potassium salt is acidified, *ethyl α-cyano-β-cyclobutylformylacetate* (V) is precipitated, and from this compound *cyclobutanecarboxylic acid* and *malonic acid* can be prepared by hydrolysis:



The experiments recorded are of interest as showing the relative stability of the *cyclopropane* and *cyclobutane* rings under precisely similar conditions. The subject has been fully discussed by Perkin and Simonsen in two recent papers (*Trans.*, 1907, **91**, 816; 1909, **95**, 1166), and as our knowledge of these compounds increases, it becomes evident that any generalisation respecting the stability

and ease of formation of the alicyclic systems must take into account not merely the formation of the rings as such, but also the influence exerted by the groups substituting the carbon atoms composing the rings. We have at the present time a series of experiments in progress which it is hoped will throw further light on this question.

EXPERIMENTAL.

Ethyl 1-Cyanocyclobutane-1-carboxylate,

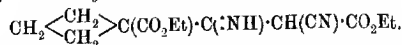
This substance was originally prepared by Carpenter and Perkin by the action of bromocyclobutane on the sodium compound of ethyl cyanoacetate (Trans., 1899, 75, 930). The compound prepared by them gave, however, figures on analysis (C=58.59; H=7.04. $\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ requires C=62.7; H=7.2 per cent.) which clearly showed, as they remarked, that it must have contained nearly 50 per cent. of ethyl cyanoacetate. We have prepared a quantity of this mixture in the manner described by Carpenter and Perkin, and find that it is quite impossible, even by repeated fractionation, to separate the cyclic ester from ethyl cyanoacetate, which always accompanies it. Recently (this vol., p. 1002), we had occasion to prepare pure ethyl 1-cyanocyclopropane-1-carboxylate, and found that it could be separated from ethyl cyanoacetate by adding the calculated quantity of sodium ethoxide to the mixture to form the sodium derivative of ethyl cyanoacetate, and then by adding water to form the soluble sodium salt of cyanoacetic acid, leaving the pure cyclic ester undissolved.

We have now applied this method successfully for the preparation of pure ethyl 1-cyanocyclobutane-1-carboxylate in the following way. The mixed esters prepared by Carpenter and Perkin's method were fractionally distilled, and the fraction boiling at 214° was analysed. (Found, C=59.21. $\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ requires C=62.7. $\text{CH}_3\text{O}_2\text{N}$ requires C=53.1 per cent.) The mixture therefore contained approximately 37 per cent. of ethyl cyanoacetate. One hundred grams were therefore added to a well-cooled solution of 7.6 grams of sodium in 100 grams of alcohol, and the product was diluted with water. The oil which then separated was extracted by ether, and the residue left after evaporating the dried ethereal solution was distilled. Pure *ethyl 1-cyanocyclobutane-1-carboxylate* is a clear, colourless liquid, boiling at $218^\circ/762$ mm.:

0.2119 gave 0.4856 CO_2 and 0.1392 H_2O . C=62.51; H=7.3.

$\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ requires C=62.7; H=7.2 per cent.

Ethyl β-imino-α-cyano-1-carbethoxy-β-cyclobutyl-1-propionate,



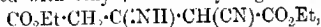
This substance was prepared by the condensation of ethyl sodium cyanoacetate with ethyl 1-cyano*cyclobutane*-1-carboxylate in the following manner. 2.3 Grams of sodium were dissolved in 30 grams of alcohol, and the solution, after being mixed with 11.3 grams of ethyl cyanoacetate, was treated with 15.3 grams of ethyl 1-cyano*cyclobutane*-1-carboxylate, and the whole heated on the water-bath for three hours. At the end of this time the dark-coloured, gelatinous product was mixed with water, and after the solution had been rendered faintly acid by acetic acid, it was distilled in a current of steam until the distillate was free from oil. The non-volatile residue, which solidified on cooling, was collected and crystallised from alcohol, from which solvent it separated in small, rectangular plates, melting at 111°:

0.1861 gave 0.4007 CO₂ and 0.1151 H₂O. C=58.7; H=6.87.

0.2012 „ 18.0 c.c. N₂ at 9° and 757 mm. N=10.7.

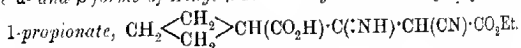
C₁₃H₁₅O₄N₂ requires C=58.6; H=6.8; N=10.5 per cent.

If the mixture of ethyl 1-cyano*cyclobutane*-1-carboxylate and ethyl cyanoacetate is used in this experiment instead of the pure cyclic ester, the product always consists of the above cyclic imino-compound mixed with ethyl β-imino-α-cyanoglutarate,



which has been formed by the condensation of ethyl cyanoacetate with its sodium derivative. The mixture may be separated by means of boiling sodium carbonate solution, which hydrolyses ethyl β-imino-α-cyanoglutarate to the sodium salt of ethyl hydrogen β-imino-α-cyanoglutarate, and leaves the cyclic imino-compound unchanged.

The α- and β-forms of Ethyl β-imino-α-cyano-1-carbory-β-cyclobutyl-1-propionate,



The two forms of this ethyl hydrogen salt are produced by the action of potassium hydroxide on ethyl β-imino-α-cyano-1-carbethoxy-β-cyclobutyl-1-propionate, the α-form at low temperatures, the β-form when the reaction is carried out at the temperature of boiling water. The conditions found most suitable for their production were as follows.

α-Form.—Ethyl β-imino-α-cyano-1-carbethoxy-β-cyclobutyl-1-propionate slowly dissolves when shaken with a solution containing rather more than the calculated quantity of potassium hydroxide

dissolved in three times its weight of water, and if, when all has passed into solution, hydrochloric acid is cautiously added until an acid reaction is obtained, an oil separates which solidifies on being scratched. When crystallised from warm water, this form of the ethyl hydrogen salt is obtained in colourless needles, which melt at 75° , and lose carbon dioxide at a higher temperature:

0.1798 gave 0.3633 CO_2 and 0.0927 H_2O . $\text{C}=55.1$; $\text{H}=5.72$.

$\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{C}=55.4$; $\text{H}=5.8$ per cent.

The α -form is very unstable, and readily gives off carbon dioxide; even when an aqueous solution of it is boiled, considerable decomposition ensues.

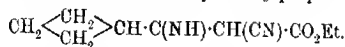
β -Form.—Some of this modification always accompanies the α -form, and can be obtained from the mother liquors employed in its recrystallisation. It can be prepared as chief product by using the following conditions. Ethyl β -imino- α -cyano-1-carbethoxy- β -cyclobutyl-1-propionate is suspended in boiling water, and rather more than the calculated quantity of aqueous potassium hydroxide added to the hot liquid. The ester quickly dissolves, and the solution is then cooled and acidified, when crystals separate at once. When recrystallised from hot water, the small prisms of the β -form are obtained, which melt and evolve carbon dioxide at 156° :

0.1790 gave 0.3649 CO_2 and 0.0937 H_2O . $\text{C}=55.6$; $\text{H}=5.8$.

$\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{C}=55.4$; $\text{H}=5.8$ per cent.

The β -form of the ethyl hydrogen salt is very stable, and can be boiled with water for a considerable time without undergoing change. The alkali salt of the α -form is completely transformed into the alkali salt of the β -modification when its aqueous solution is boiled, but the reverse change could not be effected.

Ethyl β -Imino- α -cyano- β -cyclobutylpropionate,



This substance is formed when either the α - or β -form of ethyl imino- α -cyano-1-carboxy- β -cyclobutyl-1-propionate is heated until the evolution of gas has ceased. The operation is conducted in a test-tube heated in a bath of sulphuric acid, and when all carbon dioxide has been evolved, the residue, which solidifies on cooling, is crystallised from dilute methyl alcohol. The imino-compound forms slender needles, which melt at 105° :

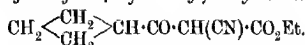
0.1821 gave 0.4125 CO_2 and 0.1203 H_2O . $\text{C}=61.78$; $\text{H}=7.34$.

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=61.9$; $\text{H}=7.2$ per cent.

Ethyl β -imino- α -cyano- β -cyclobutylpropionate is a tautomeric imino-amino(ketimino-enamic)-derivative, which is slowly hydrolysed

by dilute mineral acid to the corresponding ketone. It is also readily hydrolysed by aqueous alkali hydroxides, forming the stable alkali salt of the enolic form of the ketone.

Ethyl α -Cyano- β -cyclobutylformylacetate,



This substance can be prepared by the action of dilute sulphuric acid on the last-named imino-compound, but is more conveniently produced by the action of aqueous potassium hydroxide. Five grams of the imino-compound are mixed with water, and slightly more than the calculated quantity of aqueous potassium hydroxide is added. The imino-compound rapidly dissolves when the solution is warmed, ammonia being evolved at the same time, and if, when all has passed into solution, it is rendered acid by hydrochloric acid, an oil is precipitated which can be extracted by ether. It is advisable, in order further to purify the ketone, to shake the ethereal solution with aqueous sodium carbonate, and then to recover the ketone by acidifying the alkaline extract and extracting it again with ether. *Ethyl α -cyano- β -cyclobutylformylacetate* is a colourless oil, which boils at $182^\circ/25$ mm.:

0.2077 gave 0.4676 CO_2 and 0.1270 H_2O . $\text{C}=61.41$; $\text{H}=6.8$.

$\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C}=61.5$; $\text{H}=6.7$ per cent.

The ester dissolves readily in aqueous alkali hydroxides and in solutions of alkaline carbonates. It gives an intense red coloration in alcoholic solution with ferric chloride.

The silver salt separates as a microcrystalline precipitate when the calculated quantity of silver nitrate solution is added to a neutral solution of the ammonium salt of the ketone:

0.2973 gave 0.1062 Ag. $\text{Ag}=35.72$.

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{NAg}$ requires $\text{Ag}=35.76$ per cent.

The salt rapidly becomes coloured on exposure to light.

Formation of cyclobutane-1: 1-dicarboxylic Acid and Malonic Acid from Ethyl β -Imino- α -cyano-1-carbethoxy- β -cyclobutyl-1-propionate.

This decomposition was effected by boiling 7 grams of the imino-compound with 20 per cent. sulphuric acid for four hours; the resulting clear solution was then distilled in a current of steam until the odour of cyclobutanecarboxylic acid, which resembles that of isobutyric acid, ceased to be apparent, and the distillate showed a neutral reaction. The non-volatile residue was then saturated with ammonium sulphate, and extracted repeatedly with ether. The dried ethereal extract, on evaporation, left a residue which

solidified. This was found to consist of a mixture of *cyclobutanecarboxylic acid* and *malonic acid*, and was separated by treatment with concentrated hydrochloric acid, in which the cyclic acid is insoluble. The pure acid was obtained in prisms, melting and decomposing at 155° . (Found, $C=49.98$; $H=5.73$. Calc., $C=50.0$; $H=5.5$ per cent.)

Malonic acid was recovered from the mother liquors used in the separation of the above acid by evaporating them to dryness and extracting the residue with ether. It was characterised by its conversion into acetic acid on distillation.

Formation of cyclobutanecarboxylic Acid and Malonic Acid from Ethyl α -Cyano- β -cyclobutylformylacetate.

Some *cyclobutanecarboxylic acid* is formed in the hydrolysis just described, and can be recovered from the steam distillate. The quantity is, however, very small, being only about 3 per cent. of the amount of imino-compound hydrolysed. The cyclic acid can, however, be prepared in quantitative yield from ethyl α -cyano- β -cyclobutylformylacetate in the following manner. Ten grams are boiled with 20 per cent. sulphuric acid for four hours, when the acid solution is distilled in a current of steam until the distillate ceases to be acid. The distillate is then saturated with ammonium sulphate and extracted with ether. The dried ethereal extract leaves a residue on evaporation which distils at 191° , and possesses characteristic odour resembling that of *isobutyric acid*. The acid was converted into its silver salt, which crystallises from hot water in long needles. (Found, $Ag=52.3$. Calc., $Ag=52.2$ per cent.)

The non-volatile portion from the steam distillate was saturated with ammonium sulphate and extracted with ether. The residue, on evaporating the ether, melted at 132° , and was proved to be malonic acid by converting it into acetic acid by distillation.

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CCXLIX.—*The Wet Oxidation of Metals. Part I.
The Rusting of Iron.*

By BERTRAM LAMBERT (Goldsmiths' Research Student) and
JAMES CAMPBELL THOMSON.

THE work of Moody (Trans., 1906, **89**, 720) and Friend (Proc., 1910, **26**, 179) would seem to point to the fact that ordinary "commercial" iron can, in some circumstances, be kept for a considerable time without undergoing visible oxidation in contact with water and air freed from acid gases, such as carbon dioxide.

These experiments are perhaps generally accepted as strong evidence in support of an explanation of the rusting of iron which was originally put forward by Crum Brown in 1888. His theory is that the rusting of iron is due primarily to the interaction between iron, carbon dioxide, and water, with the formation of ferrous bicarbonate, which then reacts with oxygen to form ferric oxide.

The impurities contained in the best commercial iron must, from a chemical point of view, be regarded as considerable, and, in the light of our present knowledge of the great modifications capable of being produced in the properties of substances by the presence of even minute traces of impurities, it cannot be contended that experiments with impure iron afford trustworthy grounds for a satisfactory theory of the oxidation of iron.

The aim of the present investigation was to bring together, under the simplest possible conditions, the purest obtainable water, oxygen, and iron, in vessels which would be least likely to be acted on by any of these substances.

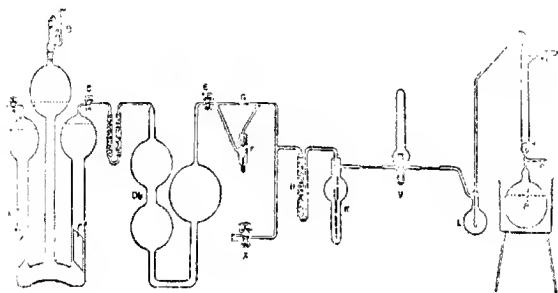
The results have been to show that chemically pure iron will not undergo visible oxidation even after long exposure to pure water and pure oxygen in vessels made of clear fused silica. Further, that a very small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions, where there is not the remotest chance of any acid substance either being present or being formed during the reaction.

Description of Apparatus: Preparation of Oxygen and Water.

Oxygen.—The oxygen used in the experiments was prepared by the electrolysis of a solution of barium hydroxide in "conductivity" water. The barium hydroxide was purified by recrystallising twelve times. The solution was electrolysed between platinum

plates in a cell *A* (Fig. 1), the air entering the reservoir of the cell, owing to changes of pressure during the electrolysis, being purified by passing through tubes containing sulphuric acid and soda-lime, as shown at *B*. The oxygen was stored in a series of flasks, *D*, of about 2 litres capacity. Before reaching the storage vessels, the oxygen was passed through a U-tube containing lumps of pure sodium hydroxide to remove the excess of aqueous vapour. This was found necessary in order to protect the lubrication of phosphoric acid on the tap *E*, which connected the oxygen storage with the rest of the apparatus. Even with this precaution, it was found that there was a slight leakage round this tap when there was a high vacuum in the rest of the apparatus. This was prevented by

FIG. 1.



introducing a mercury trap of the type shown in the figure at *F*. (The principle of this trap is explained later.)

All the taps were mercury-sealed and lubricated with glacial phosphoric acid.

Water.—The water was prepared by distillation, in a vacuum, from a concentrated solution of barium hydroxide. The barium hydroxide, purified as before, was dissolved in "conductivity" water in the flask *P*, which was separated from the rest of the apparatus by a thin bulb, *V*, sealed into a wider tube connecting with the rest of the apparatus, as shown in the figure. Connexion was made between the water supply and the rest of the apparatus, at the proper time, by causing the glass rod at *M* to drop on to the thin bulb *V* and break it.

The air in contact with the baryta solution was removed through the side-tube *O*, which was drawn out to a capillary and attached to a good water-pump. The water in the flask was then boiled vigorously, under diminished pressure, for two or three hours, the

capillary being sealed while the water was boiling. In this way all but the smallest traces of air were removed from the flask.

The "conductivity" water used to prepare the solutions of barium hydroxide for the cell *A* and the flask *P* was made by Kohlrausch's method by distillation through alkaline and acid solutions of potassium permanganate. It was condensed in a block-tin condenser, and collected and stored in a large Jena-glass flask, with arrangements for syphoning off and for protecting it from contact with impure air, as used by Hartley, Campbell, and Poole (*Trans.*, 1908, **93**, 428). Only the middle portions of the distillate were used. This water was also used in the final washing of all parts of the apparatus before they were set up.

The choice of the kind of vessel in which to carry out the experiments was the cause of much difficulty. It was finally decided to use vessels made of transparent fused silica as being least likely to be affected by either water, iron, or oxygen. After many trials and experiments, a simple form of glass vessel was devised, which, with a tube of clear fused silica, gave all the advantages of an apparatus made entirely of silica, since the water which collected in the silica tube and came in contact with the iron must have condensed on the inside of the silica tube itself. The silica tubes were about 8 cm. in length and 1 cm. in diameter, and were closed at one end.

A silica tube was made to slide loosely into an outer glass vessel, of the shape shown at *F* in the figure, and to be so supported by the lower end of the glass vessel that the open end of the tube and half its length were not in contact with the glass. The pure iron (preparation described later) was put into the silica tube, which was then placed in the outer glass vessel; the glass vessel was then closed at the top and sealed into position by means of the side-tubes connecting with the oxygen supply and the water supply, as shown in the figure. These side-tubes were drawn out to capillaries in order to facilitate the sealing off of the vessel when the experiment was finished. (Three or four such vessels were used in each experiment, and were sealed on in parallel.)

Between the vessel *I'* and the water supply was a trap *L*, to catch and retain any water which condensed before reaching this point. Between the vessel *I'* and the oxygen supply was a trap *K*, of shape shown in the figure, the use of which is explained below, and a tube *H*, containing glass-beads covered with pure gold-leaf. This device was used to protect the vessel containing the iron from contamination with mercury vapour, for, in evacuating the apparatus, a very high vacuum was obtained, and mercury was contained both in the trap *F* and in the pumps.

All joints in the apparatus were sealed glass joints, and no rubber connexions of any kind were used.

All the glass parts of the apparatus were very thoroughly cleaned and steamed, at intervals, for several hours.

The silica tubes were boiled with pure concentrated nitric acid for several weeks, and were afterwards steamed and boiled with constant changes of freshly made conductivity water for several days. They were finally heated strongly in a clear blow-pipe flame.

The whole apparatus was connected, beyond the tap *X*, with a combined Sprengel and Töpler pump and a drying tube containing phosphoric oxide.

Method of Conducting the Experiment.—The whole apparatus between the bulb *N* (separating the water supply) and the tap *C* was evacuated. The tap *E* was then closed, and the storage vessels *D* filled with oxygen made by electrolysis of the baryta in the cell *A*. The capillary at *G* was sealed, so that any slight leakage of oxygen round the tap *E* merely served to push up the mercury in the trap *F*, and did not affect the vacuum in the rest of the apparatus. The thin bulb *N* was then broken by causing the heavy glass rod *M* to fall on it. It was usually found that there was a little residual air in the flask *P*, which had not been completely removed in the boiling off process. The quantity of air was extremely small, and was easily removed by working the mercury pumps for a few minutes.

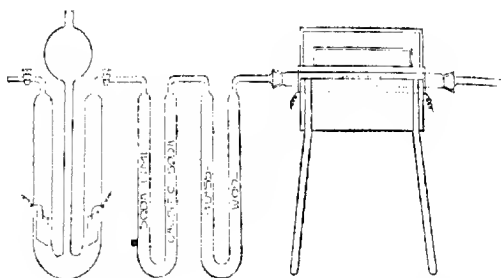
The flask *P* was then very gently heated on a water-bath, the temperature never being raised so high as to promote rapid evaporation. The first portions of water were caused to condense in the vessel *K* by surrounding it with ice. When the water collected in *K* reached a depth of about 12 cm., the lower end of the vessel *I* was cooled, and water slowly condensed inside the silica tube and in contact with the iron. The water collecting in the silica tube must necessarily have condensed only on silica; any water which condensed on the glass vessel supporting the silica tube simply running down and collecting outside the silica tube.

When a sufficient quantity of water had been obtained in contact with the iron, the capillary to the right of *I* was sealed off by means of a small flame. Oxygen was then allowed to enter the apparatus by slowly opening the tap *E*. This pure oxygen, before entering *I*, was washed by passing through the pure water collected in the trap *K* for this purpose. The capillary to the left of *I* was then sealed, thus leaving the iron in contact with pure water and pure oxygen in a sealed vessel. The vessel was put aside for observation.

Preparation of Pure Iron.—The material employed in the pre-

paration of pure iron was a pure specimen of "Kahlbaum" ferric chloride. The salt was found to be free from sulphate, arsenic, alkali, or alkaline earth metals. A solution of the salt was made in conductivity water and electrolysed between electrodes of pure iridium foil. This method is made possible by the fact that pure iridium is not attacked by chlorine, which is evolved at the anode. The metallic iron which was deposited on the cathode was then thoroughly washed with conductivity water, and dissolved in pure dilute nitric acid. This solution of ferric nitrate in excess of nitric acid was concentrated on the water-bath, and the salt crystallised from the solution in concentrated nitric acid. The crystals were separated from the mother liquor, washed with pure concentrated nitric acid, and recrystallised four or five times from this solvent. The crystals so obtained were colourless, or white when seen in bulk. It is to be noticed that ferric nitrate, prepared from ordinary pure

FIG. 2.



iron, has, when seen in bulk, a pale violet colour like that of iron alum, and that the colour cannot be removed by repeated crystallisation from pure nitric acid.

The ferric nitrate crystals were transferred by means of a spatula of iridium foil to a pure iridium boat. The boat was then heated in air on a thick tile, so that the flame gases did not come in contact with it. The ferric nitrate was thus converted into the oxide or basic nitrate. The boat containing the flakes of oxide was then placed into a transparent silica tube, and heated in an electric resistance furnace to a bright red heat (just above 1000°), while a stream of pure hydrogen was passed through the tube.* Fig. 2

* In some experiments the oxide was heated in a stream of pure oxygen for several hours before being reduced, in order to remove the occluded nitrogen which is contained in most oxides formed from nitrates. This operation, however, was found to be unnecessary, since the properties of the resulting iron were exactly the same as when the oxide or basic nitrate was directly reduced in hydrogen. The

shows the arrangement of the apparatus for this operation. The hydrogen was prepared by the electrolysis of a solution of pure barium hydroxide. The figure only shows half the electrolytic cell, which contains two pairs of large platinum electrodes and is capable of producing a steady stream of hydrogen. The gas was passed through a U-tube containing lumps of pure sodium hydroxide, in order to remove excess of water vapour, and then through another U-tube containing tightly-packed glass wool.

The metallic iron so obtained, by direct reduction of the flakes of oxide or basic nitrate, had a distinct metallic lustre and a light grey colour. If the flakes of oxide were ground in an agate mortar before being reduced, the iron produced by reduction was light grey in colour, but had little or no lustre. The properties of the two kinds of iron were the same.

The Jena-glass beakers used in the preparation of the ferric nitrate were thoroughly cleaned and boiled out for several weeks with constant changes of pure concentrated nitric acid. They were also steamed out at intervals for several hours. The same treatment was applied to a Gooch crucible, which was used for separating and washing the ferric nitrate crystals. The iridium boat was boiled for several weeks with aqua regia and then with concentrated nitric acid; it was finally heated to a high temperature in a stream of hydrogen in the electric resistance furnace.

The nitric acid used throughout in the preparation of ferric nitrate was made by the distillation, under diminished pressure, of a pure commercial nitric acid. The acid was distilled twice, the first and last portions of the distillate being discarded in both cases.

Fig. 3 shows the apparatus which was used for the distillation of the nitric acid. The acid was introduced into the distilling flask *A* by means of the side-tube *B*, which was then sealed off. The connexions between distilling flask, condenser, and receiver were sealed joints. Nitric acid distilled under low pressure is very liable to froth violently, and so a large trap was introduced at *C*. A good water-pump was used to evacuate the apparatus through the tap *D*. The acid was drawn off through the tube *E* by cutting off a small portion of the capillary, which was sealed up again immediately afterwards. After this apparatus had been used for several weeks and the surface alkali had been dissolved from the glass, the nitric acid obtained was very pure, and 30 c.c. left no weighable residue when evaporated to dryness on the water-bath. The product

slight surface oxidation undergone by the iridium did not seem to affect the iron. The occluded nitrogen was undoubtedly removed by heating in hydrogen to the high temperature of the furnace. This temperature was between the melting point of silver and that of copper.

obtained by distilling nitric acid from a platinum retort was not nearly so good.

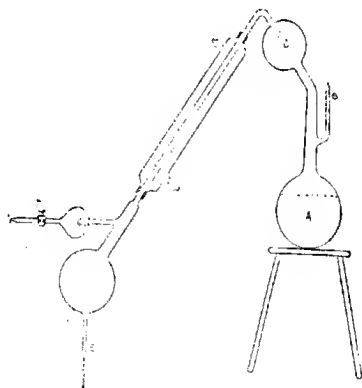
It is to be noticed that throughout the preparation of pure iron the use of platinum apparatus was avoided.

Results of Experiment and Conclusions.

It was found that pure iron, prepared exactly as described above, did not undergo any visible oxidation when treated with pure water and pure oxygen in vessels made of clear fused silica, and that there was no change even after several months.

If, however, ferric nitrate, prepared from ordinary pure iron, was used, even after ten recrystallisations, and iron made from it

FIG. 3.



by precisely the same method, the iron invariably showed signs of oxidation in two or three hours, and, after twelve hours, there was always a considerable deposit of reddish-yellow ferric oxide on parts of the metal. Oxidation also took place even when the oxide prepared from the nitrate was strongly heated in a stream of pure oxygen for several hours before being reduced to the metal.

It is impossible that iron prepared in this way can contain anything more than a very slight trace of impurity, and that impurity, whatever it may be, cannot be of such a nature that it is acid, or will give an acid on oxidation.

Again, if platinum vessels were used, particularly if a platinum boat was used in which to reduce the iron, the iron produced readily underwent oxidation in two or three hours, and oxidation invariably took place at those parts of the metal which had been heated in contact with the platinum boat.

Richards (*Proc. Amer. Acad.*, 1900, 35, 253), in his work on the atomic weight of iron, prepared iron in somewhat the same way as we have done, but he distilled the nitric acid used from a platinum retort, and employed platinum vessels throughout for his preparation. He states that the iron always contained slight traces of platinum, and that, when it was dissolved in acids, a small black speck of platinum remained.

This small trace of platinum, which may be merely attached to the iron, or may be present in the form of a solid solution, would seem to be enough to cause oxidation to take place.

All kinds of commercial iron which were used readily rusted under the same conditions of experiment, as also did iron made with the most scrupulous care by many other methods.

A specimen of commercial electrolytic sheet iron (99.9 per cent. of iron), which had been polished and treated with a 1 per cent. solution of chromic acid for three months, and afterwards washed with pure water and quickly dried, readily rusted under the same conditions of experiment. This method of treating ordinary iron is said by Moody to remove the impurities from the surface of the iron. It seems probable that other reasons must be sought for the non-rusting of the commercial iron used by Moody under his precise conditions of experiment.

It would seem to be proved from these experiments that pure iron will not undergo visible oxidation in contact with pure water and pure oxygen, but that a small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions of experiment, even if this impurity be not of an acid nature or likely to produce an acid during the reaction.

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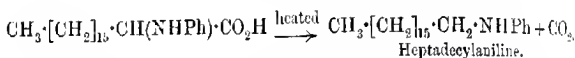
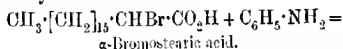
(VI.—*Preparation of Secondary Amines from Carboxylic Acids. Part I. Preparation of Heptadecylaniline, Pentadecylaniline, and Tridecylaniline.*

By HENRY RONDEL LE SUEUR.

THE method most generally employed for the preparation of secondary amines consists in the interaction of an alkyl haloid compound and a primary amine. A serious objection to this method is that tertiary amines are also formed, and the subsequent

separation of the secondary amines from these is a matter of considerable difficulty. Further, this method necessitates the use of alkyl monohaloid compounds, and these, with the exception of the lower members, are not always easy to prepare.

The method which is now brought forward for the preparation of monoalkylanilines, and which, so far as can be ascertained, is new, is free from these two objections, as, firstly, owing to the nature of the reaction, there is no possibility of the formation of dialkyl-anilines, and, secondly, the entering alkyl group results directly from an acid, and acids are more easily obtained than any other class of organic compounds. The new method is briefly as follows: (1) the α -anilino-acid is prepared by the interaction of aniline and the α -bromo-acid, (2) the α -anilino-acid is heated to considerably above its melting point, whereby it loses carbon dioxide, and a monoalkylaniline results:



In the three cases so far investigated, and which form the subject of this communication, the yield of α -anilino-acid was more than 70 per cent. of the theoretical, and the yield of alkylaniline was also more than 70 per cent. of that theoretically obtainable from the anilino-acid.

α -Anilino-stearic acid, α -anilinopalmitic acid, and α -anilinomyristic acid have been already prepared by Hell and his collaborators (*Ber.*, 1889, **22**, 1748; 1891, **24**, 942, 2395), who obtained these compounds by the interaction of aniline and the respective α -bromo-acid at 180—185°. Heating to 180—185° is not necessary, and is to be avoided, as at this high temperature there is a likelihood of the anilino-acid undergoing decomposition, and also of the formation of an anilide and of an $\alpha\beta$ -unsaturated acid, the latter being formed by the removal of hydrogen bromide from the α -bromo-acid by the aniline. *Heptadecylaniline*, $\text{C}_{17}\text{H}_{33} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, *pentadecylaniline*, $\text{C}_{15}\text{H}_{31} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, and *tridecylaniline*, $\text{C}_{13}\text{H}_{27} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, are colourless solids, which melt at a low temperature, and are readily soluble in most of the common organic solvents. Their hydrochlorides are insoluble in cold water, and when heated with this liquid they melt and undergo almost complete hydrolysis into the free base and hydrogen chloride.

The author is now engaged in the investigation of the application of the above reaction to the preparation of secondary amines in

general, and more particularly of monoalkylnaphthylamines and other monoalkylanilines, and from the results so far obtained it is evident that this method is not limited to the preparation of the higher monoalkylanilines.

EXPERIMENTAL.

Preparation of α -Anilino-stearic Acid, $C_{16}H_{33}\cdot CH(NHPh)\cdot CO_2H$.

Thirty grams of α -bromostearic acid (1 mol.) and an equal weight of aniline (4 mols.) were heated together in a flask immersed in boiling water for thirteen hours. The resulting solid was thoroughly digested with excess of hot dilute hydrochloric acid, collected, and washed with dilute acid and water to remove excess of aniline; it was then dried and crystallised from a mixture of alcohol and ethyl acetate, when 23 grams of the pure acid were obtained. (Found, C=76.54; H=10.75; N=3.91. Calc., C=76.80; H=10.93; N=3.73 per cent.)

α -Anilino-stearic acid is sparingly soluble in alcohol, acetone, benzene, or chloroform in the cold, but dissolves readily on heating. It is insoluble in water, ether, or light petroleum, and separates from ethyl acetate in nodular aggregates, melting at 141–142°, and not at 84.5°, as stated by Hell and Sadomsky (*Ber.*, 1891, **24**, 2355). The low melting point given by Hell and Sadomsky is obviously not in agreement with the value to be expected from analogy to other similar α -anilino-acids.

Heptadecylaniline, $C_{17}H_{35}\cdot NH\cdot C_6H_5$.

Five grams of α -anilino-stearic acid were placed in a small flask containing a thermometer, the bulb of which dipped into the substance, and the whole heated in a metal-bath. As soon as the substance was melted, the temperature was raised rapidly to about 150°, at which point the evolution of carbon dioxide commenced. The temperature was then raised more slowly to 270–280°, and the heating stopped when the evolution of carbon dioxide had ceased. The evolution of carbon dioxide is very rapid at about 270°, and there is no evidence of charring or secondary decomposition at any stage of the heating, which for 5 grams of acid requires about fifteen minutes. The product resulting from 20 grams of anilino-acid, heated in quantities of 5 grams at one time as described above, was distilled under 50 mm. pressure, when 14.3 grams of distillate, boiling between 295° and 300°, were obtained. This was redistilled under 35 mm. pressure, and gave:

| | |
|----------------------------------|------------|
| Below 285° | 2.3 grams. |
| 285–290° | 10.0 „ |
| Undistilled residue = 2.0 grams. | |

The fraction 285—290° readily solidified to a white solid melting at 41—42°, and consisted therefore of the pure amine, and, nearly the whole of the fraction distilled at 285—286°, this temperature is to be regarded as the boiling point of the pure substance. The amine was also purified by crystallisation instead of fractional distillation, in which case the method adopted was as follows. The product resulting from the heating of the anilino-acid was distilled in a vacuum and the distillate dissolved in ether, the ethereal solution washed with a solution of potassium hydroxide, dried with solid potassium hydroxide, and the residue left on evaporation of the ether crystallised from alcohol until its melting point was constant. This alternative method of purification is especially applicable to the preparation of small quantities of the amine:

0.1632 gave 0.5000 CO_2 and 0.1836 H_2O . $\text{C} = 83.55$; $\text{H} = 12.50$.

0.2380 „ 8.7 c.c. N_2 (moist) at 12° and 770 mm. $\text{N} = 4.40$.

$\text{C}_{17}\text{H}_{35}\text{N}$ requires $\text{C} = 83.38$; $\text{H} = 12.38$; $\text{N} = 4.23$ per cent.

Heptadecylaniline is readily soluble in ether, benzene, chloroform, acetone, light petroleum, or ethyl acetate in the cold, sparingly so in cold alcohol, but readily so on warming, and crystallises from this solvent in large plates, which soon change to long needles, the latter being the stable crystalline form. Heptadecylaniline melts at 42—43°, and boils at 285—286°/35 mm. It is insoluble in hydrochloric acid, but dissolves readily in concentrated sulphuric acid.

The *hydrochloride*, $\text{C}_{17}\text{H}_{35}\text{N} \cdot \text{C}_6\text{H}_5\text{HCl}$, was obtained by dissolving 1.5 grams of the amine in 50 c.c. of ether, and passing dry hydrogen chloride into the solution until saturated. The precipitated hydrochloride was collected, washed with ether, dried, and crystallised from light petroleum (b. p. 60—80°), when it was obtained in beautiful, thin, glistening plates, melting at 99—100°. It is sparingly soluble in alcohol, ether, acetone, benzene, or light petroleum in the cold, and readily dissolves in cold chloroform or boiling light petroleum. It is insoluble in cold water; in hot water, however, the substance melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. 0.2856 Gram, suspended in hot water, required 7.8 c.c. $\text{N}/10\text{-NaOH}$ for neutralisation of the aqueous solution, using methyl-orange as indicator, whereas the same weight of the compound, $\text{C}_{17}\text{H}_{35}\text{N} \cdot \text{C}_6\text{H}_5\text{HCl}$, requires 7.8 c.c. $\text{N}/10\text{-NaOH}$.

The *acetyl* derivative, $\text{C}_{17}\text{H}_{35}\text{N}(\text{CH}_3\text{CO})\text{C}_6\text{H}_5$, was readily prepared by boiling together half a gram of the amine and two grams of acetic anhydride for one and a-half hours. The excess of acetic anhydride was removed by allowing the product to remain in a vacuum over a saturated solution of potassium hydroxide, and the

solid residue was purified by crystallisation from methyl alcohol containing a small quantity of water:

0.1600 gave 5.9 c.c. N_2 (moist) at 20° and 750 mm. $N = 3.94$.

$C_{23}H_{43}ON$ requires $N = 3.75$ per cent.

Acetoheptadecylanilide is readily soluble in most of the ordinary organic solvents, and crystallises from methyl alcohol containing a little water in feathery aggregates of slender needles, melting at $42-43^\circ$.

The *nitrosoamine*, $C_{17}H_{35} \cdot N(NO) \cdot C_6H_5$, was most easily obtained by the following method, which gave a practically theoretical yield of the pure substance. 1.5 Grams of the amine were dissolved in 10 c.c. of concentrated sulphuric acid, and this solution added drop by drop to a solution of 3 grams of sodium nitrite in 80 c.c. of water, the whole being vigorously shaken, and more (about 2 grams) sodium nitrite added from time to time. The resulting solid was collected, washed, dried, and crystallised from methyl alcohol:

0.1520 gave 10.5 c.c. N_2 (moist) at 18.5° and 760 mm. $N = 7.96$.

$C_{23}H_{43}ON_2$ requires $N = 7.78$ per cent.

Phenylheptadecylnitrosoamine is readily soluble in ether, chloroform, benzene, light petroleum, or acetone in the cold, sparingly so in cold methyl alcohol, but dissolves readily on heating, and crystallises from this solvent in light fawn-coloured plates, melting at $53-54^\circ$. A small quantity of the nitrosoamine, mixed with a little phenol and warmed with concentrated sulphuric acid, gave a blue solution, which, on dilution, gave a red, opalescent liquid, turning blue on being rendered alkaline.

Preparation of α -Anilinopalmitic Acid.

Thirty grams (1 mol.) of α -bromopalmitic acid and an equal weight ($3\frac{1}{2}$ mols.) of aniline were heated together in a flask immersed in boiling water for seven hours, and the resulting product was worked up as described for the preparation of α -anilinostearic acid (p. 2435). The crude acid was purified by crystallisation from a mixture of alcohol and ethyl acetate, and was obtained in nodules, melting at $143-144^\circ$, a melting point which agrees with that given for this substance by Hell and Jordanoff (*Ber.*, 1891, **24**, 942). The yield of pure acid obtained corresponded with 80 per cent. of the theoretical. (Found, $N = 4.09$. Calc., $N = 4.03$ per cent.)

Pentadecylaniline, $C_{15}H_{31} \cdot NH \cdot C_6H_5$

The α -anilinopalmitic acid was heated in quantities of 5 grams in a flask immersed in a metal-bath, as described for the preparation of

heptadecylaniline (p. 2435). The evolution of carbon dioxide commenced at about 190°, was rapid at 220°, and had ceased after fifteen minutes' heating, the temperature having risen at the end of that time to 280°. The product resulting from 29 grams of anilino-acid heated as described above was distilled under 40 mm pressure, when the following fractions were obtained:

| | | | |
|------------------|------------|-----------------------|------------|
| Below 274° | 2.8 grams. | 290—340° | 2.3 grams. |
| 274—290° | 17.7 „ | Undistilled residue.. | 3.0 „ |

The fraction 274—290° was redistilled under 40 mm. pressure, when 16 grams, boiling at 271—274°, were obtained, which solidified to a colourless solid, melting at 32—33°, and consisted of the pure amine. The fraction boiling below 274° on crystallisation from alcohol gave 1.6 grams of the pure substance. The total weight of pure amine obtained from 29 grams of anilino-acid was 17.6 grams, which corresponds with a 70 per cent. yield of the theoretical:

0.1488 gave 0.4548 CO₂ and 0.1640 H₂O. C = 83.35; H = 12.21.

0.2164 „ 8.8 c.c. N₂ (moist) at 18° and 762 mm. N = 4.71.

C₂₁H₃₃N requires C = 83.17; H = 12.21; N = 4.62 per cent.

Pentadecylaniline is readily soluble in ether, benzene, chloroform, acetone, light petroleum, or ethyl acetate in the cold, is sparingly soluble in cold alcohol, but dissolves readily on warming, and crystallises from this solvent in feathery aggregates, melting at 34—35°. It is insoluble in hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The pure amine boils at 271° 40 mm.

The *hydrochloride*, C₁₅H₃₁·NH·C₆H₅·HCl, was readily obtained by passing dry hydrogen chloride into a solution of 1 gram pentadecylaniline in 30 c.c. of ether, when the pure hydrochloride soon crystallised in glistening plates, which melted at 97.5°. It is insoluble in ether, acetone, benzene, or light petroleum in the cold, dissolves readily in cold chloroform and in boiling light petroleum from which it separates in glistening plates on cooling. It is insoluble in water, and when heated with this solvent it melts but does not dissolve, the water acquiring a strongly acid reaction.

0.2574 Gram, suspended in hot water, required 7.50 c.c. N/10 NaOH for neutralisation, using methyl-orange as indicator, where the same weight of the compound C₁₅H₃₁·NH·C₆H₅·HCl requires 7.58 c.c. N/10 NaOH.

The *acetyl* derivative, C₁₅H₃₁·N(CH₃·CO)·C₆H₅, was prepared by boiling 1 gram of the amine with 4 grams of acetic anhydride for four hours. The excess of anhydride was removed by allowing the product to remain in a vacuum over a concentrated solution of potassium hydroxide, and the residue crystallised from methyl alcohol containing a very little water:

0.008 gave 7.5 c.c. N_2 (moist) at 27.5° and 766 mm. $N = 4.14$.

$C_{23}H_{39}ON$ requires $N = 4.06$ per cent.

Acetopentadecylanilide is very readily soluble in all the common organic solvents, and crystallises from methyl alcohol containing a little water in hair-like needles, melting at 30.5–31.5°.

The *nitrosoamine*, $C_{15}H_{31}N(NO)C_6H_5$, was prepared by adding a solution of 1 gram of the amine in 8 c.c. of concentrated sulphuric acid to a dilute solution of sodium nitrite, the latter being kept in considerable excess, as described for the preparation of the nitrosoamine of heptadecylaniline (p. 2437). The crude nitrosoamine was purified by crystallisation from methyl alcohol:

0.1120 gave 10.2 c.c. N_2 (moist) at 16° and 768 mm. $N = 8.46$.

$C_{21}H_{35}ON_2$ requires $N = 8.43$ per cent.

Phenylpentadecylnitrosoamine is readily soluble in ether, chloroform, light petroleum, acetone, or benzene in the cold, and crystallises from methyl alcohol in glistening, flat needles, which melt at 49°, and have a light fawn colour. A small quantity of the nitrosoamine warmed with phenol and concentrated sulphuric acid gave a deep blue solution, which, on dilution, gave a red, opalescent liquid, turning blue on being rendered alkaline.

Preparation of α -Anilinyristic Acid.

Thirty grams (1 mol.) of α -bromomyristic acid and 32 grams (3½ mols.) of aniline were heated together in a flask immersed in boiling water for eight hours. The product was worked up as described for the preparation of α -anilinoostearic acid (p. 2435), and the acid purified by crystallisation from a mixture of alcohol and ethyl acetate, from which it separated in nodular aggregates melting at 142–143° (compare Hell and Twerdomedoff, *Ber.*, 1889, 22, 1748). (Found, $N = 4.79$. Calc., $N = 4.39$ per cent.)

Tridecylaniline, $C_{13}H_{27} \cdot NH \cdot C_6H_5$.

The α -anilinyristic acid was heated in quantities of 5 grams in a flask immersed in a metal-bath exactly as described for the preparation of heptadecylaniline and pentadecylaniline (pp. 2435, 2437), the course of the decomposition being similar in all three cases. The product resulting from the action of heat on 16 grams of anilinyristic acid was distilled under 35 mm. pressure:

| | | | |
|----------------|-----------------|-------------------------|------------|
| 240–245° | few drops only. | 260–280° | 1.5 grams. |
| 248–253° | 10.5 grams. | Undistilled residue ... | 1.7 „ |

The fraction 248–255° was redistilled under 35 mm. pressure.

when 9.8 grams, boiling at 250–255°, were obtained, which solidified to long, flat needles, melting at 23–24°. This corresponds with a 71 per cent. yield of the theoretical. A portion boiling at 251° was collected separately for analysis:

0.1512 gave 0.4582 CO_2 and 0.1632 H_2O . $\text{C}=82.65$; $\text{H}=11.99$.

0.2052 „ 9.6 c.c. N_2 (moist) at 15° and 766 mm. $\text{N}=5.52$.

$\text{C}_{19}\text{H}_{33}\text{N}$ requires $\text{C}=82.91$; $\text{H}=12.00$; $\text{N}=5.09$ per cent.

Tridecylaniline is readily soluble in alcohol, ether, benzene, chloroform, acetone, or light petroleum, and crystallises from rectified methyl alcohol in long needles, melting at 23–24°. It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. It boils at 251°/35 mm.

The *hydrochloride*, $\text{C}_{13}\text{H}_{27}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot\text{HCl}$, was prepared by passing dry hydrogen chloride into a solution of 1.5 grams of the amine in 50 c.c. ether until saturated. Light petroleum was then added to the ethereal solution, and the ether evaporated, when, on allowing the resulting solution to cool, the hydrochloride separated in glistening thin plates. It is readily soluble in alcohol, chloroform, or benzene in the cold, is insoluble in cold acetone or ether, and crystallises from light petroleum (b. p. 60–80°) in glistening, thin plates, melting at 94.5–95.5°. When heated with water, it melts but does not dissolve, and the water becomes strongly acid.

0.3060 Gram, suspended in hot water, required 9.8 c.c. $\text{N}/10$ NaOH , using methyl-orange as indicator, whereas this amount of the compound $\text{C}_{13}\text{H}_{27}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot\text{HCl}$ requires 9.8 c.c. $\text{N}/10$ NaOH .

The *acetyl* derivative, $\text{C}_{13}\text{H}_{27}\cdot\text{N}(\text{CH}_3\cdot\text{CO})\cdot\text{C}_6\text{H}_5$, was prepared by the interaction of the amine and acetic anhydride, as described for the preparation of the other acetyl derivatives:

0.1852 gave 7.6 c.c. N_2 (moist) at 15° and 756 mm. $\text{N}=4.77$.

$\text{C}_{21}\text{H}_{35}\text{ON}$ requires $\text{N}=4.41$ per cent.

Acetotridecylanilide is readily soluble in all the common organic solvents, and crystallises from its solution in dilute methyl alcohol when cooled in a mixture of ice and salt, in flat needles, melting at 31–32°.

The *nitrosoamine*, $\text{C}_{13}\text{H}_{27}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_5$, prepared in a manner similar to the other two nitrosoamines, was crystallised from methyl alcohol:

0.1520 gave 12.5 c.c. N_2 (moist) at 19.5° and 769 mm. $\text{N}=9.41$.

$\text{C}_{19}\text{H}_{31}\text{ON}_2$ requires $\text{N}=9.21$ per cent.

Phenyltridecylnitrosoamine is readily soluble in chloroform, ether, light petroleum, or benzene in the cold, sparingly so in cold alcohol,

and crystallises from methyl alcohol in fawn-coloured, glistening plates, melting at 39–40°. It gives a well-marked Liebermann's reaction, the colour changes being similar to those given by the other two nitrosoamines.

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CCLI.—*The Reduction of Chloric Acid.*

By RALPH ROSCOE ENFIELD.

THE reduction of chlorates or of chloric acid has been the subject of a considerable number of investigations. In general, it has been found that a chlorate, such as potassium chlorate, is readily reduced by zinc and sulphuric acid, but according to Tommasi (*Compt rend.*, 1903, **136**, 1005) the salt is not reduced by sodium amalgam in acid, alkaline, or neutral solutions, whilst, according to Hendrixson (*J. Amer. Chem. Soc.*, 1904, **26**, 747), the same agent has a slight reducing action.

Experiments performed in repetition of this work showed that in presence of excess of a strong acid the chlorate was readily reduced by sodium amalgam, whilst even in alkaline solution reduction could be brought about by the introduction of other metals, such as platinum, copper, iron, etc. In the latter case the effect of addition of one of the metals may be regarded as being due to its influence on the electric potential of the hydrogen evolved. The values of the E.M.F. were determined of a cell containing a solution of potassium chlorate, in which sodium amalgam was used as the anode, and a series of other metals as cathode, and the metals tabulated in the order of the numbers obtained, namely, platinum, copper, iron, nickel, lead, zinc, mercury. It was found that potassium chlorate was reduced when a cathode giving a high value of the E.M.F. was used, whilst reduction did not take place when the latter fell below a certain value.

In alkaline solution therefore reduction appears to depend on the activity of the hydrogen used as measured in terms of electric potential, a result which is in agreement with those of Tafel (*Z. physikal. Chem.*, 1900, **34**, 187) and others.

In acid solution, however, the conditions are more complex, and other factors than the activity of the hydrogen are involved. By addition of excess of sulphuric acid to a solution of potassium

chlorate, reduction is easily effected with sodium amalgam. If, on the other hand, a dilute solution of chloric acid prepared by the action of sulphuric acid on barium chlorate, and free from any other acid, is acted on by sodium amalgam, reduction is not effected, whilst in the presence of other strong acids reduction takes place. Similar results were obtained by employing other reducing agents; methyl alcohol, for example, gave no reduction after being left in contact with a dilute solution of chloric acid for a fortnight, although in the presence of sulphuric acid reduction was readily effected. Similarly, Burchard (*Zeitsch. physikal. Chem.*, 1888, 2, 823) has shown that mixed dilute solutions ($N/50$ or $N/100$) of chloric and hydriodic acids produce no iodine after keeping for several days. The case is therefore one of some complexity, and it is evident that the presence and concentration of hydrogen ions is an important factor in the reaction. The following experiments were undertaken with a view to the elucidation of this point.

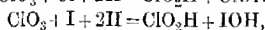
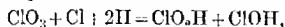
The question of the interaction of chloric acid in a solution containing some oxidisable substance has been the subject of a number of investigations. Burchard (*loc. cit.*) investigated the action of chloric, bromic, and iodic acids on hydriodic acid. He found that the reaction with chloric acid was very much slower than in the case of the other two acids, and that in order that it should proceed with a sufficient velocity it was necessary that the solutions should be so concentrated and the time of action so long that the exact nature of the reaction could not be determined. The presence of other acids in these reactions which did not take part in the reaction was found to have an accelerative effect in proportion to the "strengths" of the acids.

Pendlebury and Seward (*Proc. Roy. Soc.*, 1889, 45, 396) investigated the reaction between chloric, hydrochloric, and hydriodic acids. They found that dilute solutions of chloric and hydrochloric acids, when mixed together, slowly evolve chlorine and oxides of chlorine, that the rate varies with the quantity of chloric acid in the first place directly, as it is the substance decomposed, and in the second place with a small acceleration proportional to the quantity. Further, variation in the quantity of hydrochloric acid has an effect (1) of a secondary order as above, namely, accelerative, and (2) an effect both primary and secondary on the decomposition of chloric acid by hydrochloric acid.

Schlundt (*Amer. Chem. J.*, 1895, 17, 754) showed that in the reaction between potassium chlorate, potassium iodide, and hydrochloric acid, the effect of increase of concentration of potassium iodide was about the same as an equivalent increase in concentration of potassium chlorate, but increase of the acid caused

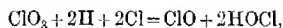
a greater increase in velocity. He further investigated the influence of other acids, and found that they exerted an accelerative influence in the order: hydrobromic, hydrochloric, nitric, and sulphuric.

Bray (*J. Physical Chem.*, 1903, **7**, 92) found that the rate at which iodine is liberated from a mixture of potassium chlorate, potassium chloride, potassium iodide, and hydrochloric acid is proportional to the concentration of the chlorate and to the square of the concentration of hydrogen ions, and is a linear function of the concentration of chlorine and of potassium iodide; this corresponds with the equations:

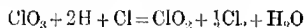


followed by instantaneous oxidation of the hydriodic acid by their products.

A similar investigation was made by Sand (*Zeitsch. physikal. Chem.*, 1904, **50**, 465), who measured the rate of liberation of chlorine from a mixture of potassium chlorate and hydrochloric acid at 70°, and found the reaction to be quinquemolecular, corresponding with the equation:



he hypochlorous acid then reacting instantaneously with hydrochloric acid to produce chlorine. On the other hand, Luther and McDougal (*Zeitsch. physikal. Chem.*, 1906, **55**, 477) find that the reaction velocity of a mixture of chloric and hydrochloric acids is inversely proportional to the square root of the concentration of chlorine, and consider that the reaction:



is involved.

It is evident from the above that the decomposition of chloric acid is not of a simple nature, especially in view, also, of the unsatisfactory results obtained when it is attempted to apply the ordinary equations for the order of reactions to this decomposition.

In this it is analogous to the case of bromic acid investigated by Ostwald, Meyerhoffer, and others.

It seemed probable to the author of the present communication that the complexity of these reactions was due to the nature of the accelerative influence of the acid, other than chloric, present in solution. Consideration of some of the preliminary experiments noted above led to the hypothesis that the reduction of chloric acid might involve the decomposition of the non-ionised molecule of chloric acid as the first stage of the reaction. If this were the case, addition of a second acid should increase the velocity of reduction of chloric acid by suppressing its ionisation, and consequently increasing the concentration of non ionised chloric acid.

It was shown by Burchard and by Schlundt that the effect of adding acids, such as sulphuric and nitric, was to stimulate the reaction in the order of the strengths of the acids. In view of the considerations just mentioned, such stimulating effect may be due (1) to the mass-action of the second acid in suppressing the ionisation of the chloric acid, or (2) to the purely catalytic influence of the hydrogen ions, the concentration of which is increased by addition of the second acid, or (3) to both. Moreover, when hydrochloric acid is the second acid employed, and the solutions are moderately concentrated, the conditions are still further complicated, since the hydrochloric acid has apparently both a primary influence (that is, it takes part directly in the decomposition of the chloric acid) and a secondary (catalytic) influence.

The following experiments on the velocity of reduction of chloric acid were made with the view of elucidating the nature of the stimulating effect of the second acid. Considerable difficulty was experienced in finding a suitable reaction owing to the extreme slowness of the decomposition, chloric acid being very much more stable than bromic acid at the same concentrations, and for this reason it was found impossible to use the reaction with hydriodic acid, which has been much investigated in the case of bromic acid, and which otherwise would have been comparatively easy to measure.

EXPERIMENTAL.

Preliminary experiments were made on the reduction of chloric acid with methyl alcohol in the presence of silver nitrate and a second acid, and determining the extent of the reaction by weighing the silver chloride formed. Experiments were made in which the strength of the second acid was varied, and it was found that the velocity of reduction increased with increase of the concentration of the second acid added, and that the accelerating influence of the acids was in the order of their strengths.

It was therefore attempted to establish a numerical relation between the acceleration due to the acid added and its affinity-constant, by measuring the velocity of reduction of chloric acid in presence of various accelerating acids.

In the following experiments, two reactions were measured, one in comparatively concentrated solutions (normal) and at comparatively high temperature (35°), and the other at lower concentrations and temperature (decinormal and 25°). In both cases it was found that the measurement of the reaction was a matter of considerable difficulty, and that therefore a high degree of accuracy was impossible, but it was hoped that the results would be

such as to indicate a definite relation between the acceleration and "strengths" of the acids.

The first reaction was that of chloric acid and methyl alcohol, and was conducted in the following manner.

A mixture of 20 c.c. of *N*-chloric acid, 10 c.c. of methyl alcohol, and 70 c.c. of *N*-acid was placed in a tube which was kept in a thermostat at 35°. From this, 10 c.c. were withdrawn every twenty-four hours, neutralised with chalk, filtered, washed, and the filtrate titrated with *N*/100-silver nitrate solution. Two experiments were made for each acid, and the mean of the two readings was taken.

A blank experiment was then made in which the catalysing acid was replaced by water, and the velocity of the reaction was found to be practically zero. The following table gives the readings for the four acids, nitric, sulphuric, benzenesulphonic, and oxalic (assuming in the latter case that the oxalic and chloric acids do not interact under these conditions), where x = the amount of reaction in terms of 0.1 c.c. *N*/100-silver nitrate, being in each case the mean of two readings, and the time is given in days.

| <i>Nitric Acid.</i> | | | <i>Sulphuric Acid.</i> | | |
|--|-------|---------------|---|-------|---------------|
| Time. | x . | Acceleration. | Time. | x . | Acceleration. |
| 1 | 29.5 | — | 1 | 17.5 | — |
| 2 | 54.5 | 25.0 | 2 | 28.0 | 10.5 |
| 3 | 77.5 | 24.0 | 3 | 38.5 | 10.5 |
| 4 | 100.0 | 23.5 | 4 | 48.0 | 10.1 |
| 5 | 128.0 | 24.6 | 5 | 57.0 | 9.9 |
| 6 | 152.0 | 24.5 | 6 | 68.0 | 10.1 |
| 7 | — | — | 7 | — | — |
| 8 | 201.5 | 24.5 | 8 | 89.0 | 10.2 |
| Mean acceleration ($\text{HNO}_3=100$), 100. | | | Mean acceleration ($\text{HNO}_3=100$), 42. | | |
| <i>Benzenesulphonic Acid.</i> | | | <i>Oxalic Acid.</i> | | |
| Time. | x . | Acceleration. | Time. | x . | Acceleration. |
| 1 | 19 | — | 1 | 6 | — |
| 2 | 33 | 14.0 | 2 | 8 | 2.0 |
| 3 | 43 | 12.0 | 3 | 8 | 1.0 |
| 4 | 59 | 13.3 | 4 | 13 | 2.3 |
| 5 | 72 | 13.2 | 5 | 13 | 1.8 |
| 6 | — | — | 6 | 14 | 1.6 |
| 7 | 94 | 12.5 | 7 | 20 | 2.3 |
| Mean acceleration ($\text{HNO}_3=100$), 53. | | | 8 | 21 | 2.1 |
| | | | Mean acceleration ($\text{HNO}_3=100$), 7.8 | | |

In the blank experiment, without addition of acid, it was found that after thirteen days the amount of reaction was equivalent to 0.5 c.c. *N*/100-silver nitrate solution, and therefore in calculating the accelerations due to the presence of the above acids at any time it was assumed that the corresponding amount of action in the blank experiment was negligible. The "acceleration" may be regarded therefore as equivalent to the velocity in each case. The

values of the acceleration at any particular time were found by subtracting from the amount of reaction which had taken place at the end of that time, the corresponding amount at the end of the first day, and dividing by the time. The amount of reaction taking place during the first day was neglected owing to the unavoidable presence of a trace of chloride at the beginning of the experiment.

The acceleration constants thus obtained are in the order of the strengths of the acids used, although not numerically comparable with the affinity-constants. Close agreement, however, was not to be expected, owing to the conditions of concentration and high temperature used. It was found impossible to obtain satisfactory results with other acids, owing in some cases to the conditions of experiment, and in others to the reaction being too slow to measure.

The second reaction studied was that of chloric acid and ferrous sulphate, which took place in decinormal solution with sufficient rapidity at 25° to be conveniently measured. The experiment tube contained a mixture of 20 c.c. of *N*/10-chloric acid, 20 c.c. of *N*/5-ferrous sulphate solution, and 60 c.c. of *N*/10-acid. After mixing, 10 c.c. were withdrawn and titrated with potassium permanganate, the titration repeated, the experiment tube containing the mixture placed in a thermostat at 25°, and the time noted. After a period of forty-five minutes, 10 c.c. were withdrawn and titrated. The reading was repeated, and the mean value recorded. Some difficulty was experienced in obtaining a good end-point in the permanganate titration owing to the presence of a small quantity of hydrochloric acid produced by the reduction of the chloric acid. It was attempted to use a large excess of manganese sulphate, but extreme difficulty was experienced in judging the colour in presence of the solution of this salt, and it was finally found more accurate to dilute the solution largely with water and to titrate in a porcelain dish, judging the colour by looking through a depth of the liquid.

The solution of chloric acid was prepared as before by the action of sulphuric acid on barium chlorate, the barium sulphate being removed by filtration. The solution was tested for excess of sulphate or barium, and then standardised with *N*-potassium hydroxide. The ferrous sulphate was prepared by dissolving pure crystals of the salt in water free from air, the solution being kept out of contact with air under a layer of benzene.

A blank experiment was made in which the accelerating acid was replaced by water, and the acceleration due to each acid was found by subtracting the amount of reaction which had taken

place in time T in the blank experiment from the corresponding amount in each of the "acid" experiments. The results were tabulated, and the acceleration constants reduced to $\text{HCl}=100$. The results obtained were as follows, where A =original concentration of ferrous sulphate in terms of 0.1 c.c. $N/100$ -permanganate, and is the mean of two readings, and x_1 , x_2 are the readings for the concentration after time T , X being the mean; T =forty-five minutes.

| Acid. | A . | x_1 . | x_2 . | X . | $A - X$. | Acceleration. | Acceleration, $\text{HCl}=100$. |
|---|-------|---------|---------|-------|-----------|---------------|----------------------------------|
| No acid | 426.5 | 375 | 376 | 375.5 | 51.0 | — | — |
| HCl | 422.0 | 248 | 247 | 247.5 | 174.5 | 123.5 | 100 |
| HBr | 430.0 | 245 | 247 | 246.0 | 184.0 | 133.0 | 108 |
| HNO_3 | 422.5 | 265 | 266 | 265.5 | 157.0 | 106.0 | 86 |
| H_2SO_4 | 425.0 | 279 | 286 | 282.5 | 142.5 | 91.5 | 74 |
| $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ | 426.0 | 257 | 256 | 256.5 | 169.5 | 118.5 | 97 |
| $\text{CH}_3\text{CO}_2\text{H}$ | 425.0 | 265 | 265 | 265.0 | 160.0 | 109.0 | 88 |
| $\text{CHCl}_2\text{CO}_2\text{H}$ | 427.5 | 328 | 329 | 328.5 | 99.0 | 48.0 | 39 |
| $\text{CH}_2\text{ClCO}_2\text{H}$ | 426.0 | 362 | 360 | 361.0 | 65.0 | 14.0 | 11 |

The acceleration constants thus obtained, compared with the corresponding affinity constants found by the hydrolysis of methyl acetate, are as follows:

| | Acceleration constant. | Hydrolysis. |
|---|------------------------|-------------------------------|
| HCl | 100 | 100 |
| HBr | 108 | 98 or 111 by sugar inversion, |
| HNO_3 | 86 | 92 |
| H_2SO_4 | 74 | 74 |
| $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ | 97 | 98 |
| $\text{CH}_3\text{CO}_2\text{H}$ | 88 | 68 |
| $\text{CHCl}_2\text{CO}_2\text{H}$ | 39 | 23 |
| $\text{CH}_2\text{ClCO}_2\text{H}$ | 11 | 4.3 |

The agreement between the acceleration constant and affinity constant is as close as would be expected, considering the nature of the reaction investigated, except in the case of the chloroacetic acids. It was thought that the high result obtained in each case with these acids might be due to the presence of hydrochloric acid formed by their hydrolytic decomposition, but the solutions were tested after the experiment with silver nitrate solution, and gave no precipitate.

The effect of variation in quantity of the catalysing acid was then examined with the view of ascertaining whether the velocity was affected in any marked degree by the presence of small quantities of the acid.

The experiments were conducted as in the last series.

The experiment tube contained a mixture of 20 c.c. of $N/10$ -chloric acid and 20 c.c. of $N/5$ -ferrous sulphate solution, and a variable quantity of sulphuric acid dissolved in 60 c.c. of water, making a total of 100 c.c.

The following results were obtained:

| No. of mols. H_2SO_4 to 1 mol. HClO_3 | A. | x_1 . | x_2 . | X. | A - X. | Accelera- tion. |
|---|-------|---------|---------|-------|--------|--------------------|
| 3 | 425 | 279 | 286 | 282.5 | 142.5 | 91.5 |
| $\frac{1}{2}$ | 418 | 343 | 345 | 344 | 74 | 29.0 |
| $\frac{1}{3}$ | 417.5 | 354 | 355 | 355 | 62.5 | 11.5 |
| $\frac{1}{7.5}$ | 417 | 360 | 361 | 360.5 | 56.5 | 5.5 |

Finally, experiments were made on the influence of neutral salts on the velocity of the same reaction. The conditions of experiment were the same as before; the experiment tube in each case contained 20 c.c. of *N*/10-chloric acid, 20 c.c. of *N*/5-ferrous sulphate solution, and 60 c.c. of an *N*/10-solution of the salt.

The following results were obtained:

| Salt. | A. | x_1 . | x_2 . | X. | A - X. | Accelera- tion. |
|--------------------------------|-------|---------|---------|-------|--------|--------------------|
| KCl..... | 415.0 | 363 | 364 | 363.5 | 51.5 | 0.5 |
| KNO_3 | 411.0 | 357 | 357 | 357.0 | 54.0 | 3.0 |
| Na_2SO_4 | 413.0 | 374 | 375 | 374.5 | 38.5 | -12.5 |
| K_2SO_4 | 416.5 | 379 | 378 | 378.5 | 38.0 | -13.0 |
| KClO_3 | 398.0 | 263 | 265 | 264.0 | 134.0 | 83.0 |
| NaClO_3 | 410.0 | 276 | 278 | 277.0 | 133.0 | 82.0 |

It is evident from these results that a neutral salt containing no common ion accelerates the reaction to a very small degree, whilst a salt containing a ClO_3 ion accelerates it very considerably. In order further to examine the reaction with a solution of potassium chlorate, an experiment was made under the same conditions as before, in which no chloric acid was present, the experiment tube containing 20 c.c. of *N*/5-ferrous sulphate solution and 80 c.c. of *N*/10-potassium chlorate solution, but it was found that the amount of reaction after forty-five minutes was practically nil. The influence of potassium and sodium sulphates on the velocity of the reaction is somewhat remarkable. Both salts retard the reaction and approximately to the same degree. This may, perhaps, be due to the formation of less easily oxidisable complex molecules with the ferrous sulphate analogous to ferrous ammonium sulphate.

Summary and Conclusions.

- (1) Chloric acid is not reduced by sodium amalgam in dilute solutions, but is reduced in the presence of strong acids.
- (2) A dilute solution of chloric acid in the presence of methyl alcohol is not reduced even when the mixture is kept for several days, but in the presence of strong acids reduction takes place.
- (3) The rate of reduction of chloric acid by methyl alcohol is extremely slow even in normal solutions, but is accelerated by

addition of strong acids, the order in which these acids accelerate the reaction being that of their relative "strengths."

(4) The reaction between chloric acid and ferrous sulphate in decinormal solution is accelerated by the addition of other acids, the acceleration produced being a function of the "strengths" of the acids.

(5) The same reaction is accelerated in a small degree by neutral salts containing no ion common with any taking part in the reaction. It is accelerated in a large degree by chlorates, and is retarded by sulphates.

It has been suggested above that the accelerative influence of the second acid may be of two kinds, and hence that this influence may be open to two theoretical interpretations. On the one hand, the reaction may be "ionic," the reduction being that of the ClO_3 ion, and the influence of addition of other acids being due to the purely catalytic influence of hydrogen ions. On the other hand, the primary reaction may be the breaking down of the non-ionised chloric acid molecule, which would be accelerated by the addition of other acids in virtue of the mass-action of the hydrogen ions. With regard to the addition of neutral chlorates, it has been shown above that these accelerate the reaction to a considerably greater degree than salts containing no ion common with any of those taking part in the reaction. This accelerative influence is similarly open to both interpretations; it may be due to the mass-action of the ClO_3 ion by which the concentration of the non-ionised chloric acid would be increased, or, since hydrogen ions are present, it may be due to the increase of total concentration of the substance undergoing reduction, namely, the ClO_3 ion. It is evident, however, that free acid is essential to the reaction, since a neutral chlorate does not appear to be affected by the reducing agents employed. Hence, if the reaction is "ionic," it must be assumed that in the absence of catalysing hydrogen ions, the reaction is too slow to measure.

With regard to the experiments given in the present communication, the most important evidence is in the relation of acceleration constants to affinity constants. Chloric acid, according to the conductivity measurements of Ostwald, is a strong acid having an affinity constant of 98, compared with 100 for hydrochloric acid. In view of this, and in view also of the great uncertainty of behaviour of strong acids in presence of their salts (and in general of solutions of mixed strong electrolytes containing a common ion), it is improbable that any close agreement would exist between the acceleration and affinity constants of the acids if the accelerative effect were due to the mass-action of hydrogen ions. Hence the

above results seem to favour the view that the reaction is an ionic one, and that the accelerative influence of the second acid is due to the catalytic action of the hydrogen ions.

Several attempts were made to devise an experiment which would exclude one or the other of the above interpretations, such as the use of a non-ionising solvent, an experiment which would have been of great value in deciding the point. Although many solvents were tried, however, none was found which would meet the requirements of the experiment.

In conclusion, I wish to express my sincere thanks to Dr. H. J. H. Fenton for valuable criticism and advice.

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CCLII.—*The Addition of Bromine to Unsaturated Compounds. Part II.*

By JOHN JOSEPH SUDBOROUGH and JOHN THOMAS.

IN continuation of the work already published (this vol., p. 715) we have examined the rate of addition of bromine to the following acids: Cinnamylidene- and *all*cinnamylidene-acetic acid, sorbic acid, δ -phenyl- Δ^a -, $-\Delta^b$ -, and $-\Delta^c$ -pentenoic acids, hydrosorbic acid, crotonic, angelic, tiglic, β -dimethylacrylic, and trimethylacrylic acid.

The method of procedure was exactly the same as that used in the earlier work, and the carbon tetrachloride and bromine were purified in the same manner. A control experiment made with brassidic acid gave values for K varying from 3.0 to 6.9, as compared with the previous values, 3.1 to 7.4. Although the new bromine and carbon tetrachloride gave values for brassidic acid which were very similar to the values obtained previously, it was found that when cinnamic acid was used, the values obtained were considerably lower than the earlier values, namely, 1.02×10^{-5} to 2.94×10^{-5} , as compared with 0.9×10^{-4} to 2.6×10^{-4} . We have not been able to ascertain the reason for this difference, but we have been able to show that the presence of moisture facilitates the addition of bromine. This is best shown in the case of the experiments with crotonic acid:

| | K . |
|--------------------------------|--|
| Dry carbon tetrachloride | 4.68×10^{-6} to 6.16×10^{-6} |
| Moist " " | 7.31×10^{-5} to 13.7×10^{-5} |

The following table gives a list of the values of K obtained for the different acids at 15°:

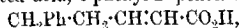
Olefine Acids.

| Acids and formula. | Series. | Maximum time. | No. of titrations. | 1/t. $x/a(a-x)$. | |
|---|---------|---------------|--------------------|-----------------------|-----------------------|
| | | | | Minimum. | Maximum. |
| Crotonic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ | a | 189 hours | 4 | 4.68×10^{-6} | 6.16×10^{-6} |
| Angelica, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ | a | 145 " | 4 | 0.83×10^{-4} | 1.9×10^{-4} |
| Thiok, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ | a | 168 " | 4 | 1.3×10^{-5} | 9.9×10^{-5} |
| 2-Dimethylacrylic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ | a | 6 " | 3 | 5.8×10^{-3} | 7.0×10^{-3} |
| Trimethylacrylic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$ | b | 6 " | 4 | 3.1×10^{-3} | 7.3×10^{-3} |
| 2-Phenyl- Δ^5 -pentenoic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 8.5 " | 4 | 1.1×10^{-2} | 2.2×10^{-2} |
| 2-Phenyl- Δ^5 -pentenoic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 0.5 " | 4 | 3.1×10^{-1} | 3.7×10^{-1} |
| 2-Phenyl- Δ^5 -pentenoic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | b | 0.5 " | 3 | 6.2×10^{-2} | 2.2×10^{-1} |
| 2-Phenyl- Δ^5 -pentenoic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 60 secs. | 4 | 45.7 | 82.3 |
| 2-Phenyl- Δ^5 -pentenoic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | b | 31 " | 4 | 35.5 | 60.3 |
| Hydrosoyic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 60 " | 4 | 1.3×10^2 | 3.3×10^2 |
| Hydrosoyic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | b | 20 " | 4 | 2.4×10^2 | 3.9×10^2 |

Diolfine Acids, with Conjugate Double Bonds.

| | | | | | |
|--|---|------------|---|-----------------------|-----------------------|
| Sorbic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 0.66 hours | 3 | 1.03×10^{-2} | 6.8×10^{-2} |
| CH ₃ CH=CH·CH=CH·CO ₂ H ... | b | 0.66 " | 4 | 1.1×10^{-2} | 12.2×10^{-2} |
| Cinnamylidenecetic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 1.0 " | 3 | 2.21×10^{-2} | 2.63×10^{-2} |
| CH ₃ CH=CH·CH=CH·CO ₂ H ... | b | 4.5 " | 4 | 0.97×10^{-2} | 1.3×10^{-2} |
| 2-Cinnamylidenecetic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | a | 1.05 " | 4 | 2.56×10^{-2} | 3.1×10^{-2} |
| 2-Cinnamylidenecetic, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$... | b | 1.25 " | 4 | 2.9×10^{-2} | 3.5×10^{-2} |

The $\alpha\beta$ -unsaturated acid, δ -phenyl- Δ^5 -pentenoic acid,



combines with bromine very slowly in the dark. Immediately after mixing, the amount of bromine used up corresponded with 0.5 c.c. of the thiosulphate solution, and even after 190 hours the amount of thiosulphate required was the same. The acid thus combines with bromine even less readily than does cinnamic acid. The following values were obtained for the two acids when the addition of bromine was allowed to take place in daylight; the two series of experiments were conducted side by side in order that the results should be strictly comparable:

Cinnamic Acid ($a=26.15$).

| t (hours). | a - x. | 1/t. $x/a(a-x)$. |
|------------|--------|-----------------------|
| 0.5 | 16.7 | 4.33×10^{-3} |
| 1.0 | 12.7 | 4.05 |
| 1.5 | 8.15 | 5.63 |
| 2.0 | 5.5 | 7.18 |

δ -Phenyl- Δ^5 -pentenoic Acid ($a=26.15$).

| t (hours). | a - x. | 1/t. $x/a(a-x)$. | t (hours). | a - x. | 1/t. $x/a(a-x)$. |
|------------|--------|-----------------------|------------|--------|-----------------------|
| 0.5 | 24.8 | 4.16×10^{-3} | 0.5 | 24.3 | 4.16×10^{-3} |
| 1.0 | 23.95 | 3.51 | 1.0 | 23.5 | 4.31 |
| 1.5 | 22.95 | 3.56 | 1.5 | 22.0 | 4.81 |
| 2.0 | 22.20 | 3.40 | 2.0 | 20.8 | 4.92 |

The results prove that in daylight bromine combines with the δ -phenyl- Δ^2 -pentenoic acid less readily than it does with cinnamic acid.

The points to which we wish to draw attention in connexion with the results tabulated above are:

(1) The values confirm the generalisation drawn previously (p. 719), namely, that $\alpha\beta$ -unsaturated acids combine with bromine far less readily than the isomerides, in which the double linking is further removed from the carboxylic group.

(2) The introduction of methyl substituents, attached to the carbon atoms between which the olefine linking exists, facilitates the addition of bromine to an appreciable extent.

(3) When the acid contains conjugated olefine linkings, one of which is in the $\alpha\beta$ -position with respect to the carboxylic group, the addition of bromine takes place more readily than when the $\alpha\beta$ -ethylene linking alone is present. In the examples we have examined, namely, sorbic, cinnamylideneacetic, and *allo*-cinnamylideneacetic acids, it is known that the two atoms of bromine are added on in the $\alpha\delta$ -positions, and the reaction is thus not strictly comparable with the addition of bromine to cinnamic acid, where the bromine attaches itself at the $\alpha\beta$ -position.

Preparation of the Acids.

1. Cinnamylidenemalonic acid was prepared by the method described by Riiber (*Ber.*, 1904, **37**, 2274), with the exception that the mixture of equal weights of malonic acid, quinoline, and cinnamaldehyde were kept in a stoppered bottle for three weeks instead of the two recommended by Riiber. The reduction of the substituted malonic acid was carried out according to Riiber's method, using pure mercury for the preparation of the amalgam, but the evolution of carbon dioxide and the formation of δ -phenyl- Δ^2 -pentenoic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was effected by a somewhat different method, as we had no method of obtaining a pressure of 0.15 mm. (*Ber.*, 1905, **38**, 2746). The dibasic acid (25 grams) was heated in a sulphuric acid bath at 110–115° until the evolution of carbon dioxide had ceased, and the product, which was slightly coloured, was distilled under a pressure of 10–12 mm., when the monobasic acid passed over at 176–182°, and solidified on cooling. The transformation of the $\beta\gamma$ -acid into a mixture of $\alpha\beta$ - and $\gamma\delta$ -unsaturated acids was carried out according to Riiber's directions (*loc. cit.*, p. 2747). The β -hydroxyphenylvaleric acid was removed by making use of its insolubility in hot carbon disulphide, and the oily acid removed by pressing the mixture of acid on a plate. The solid mass, consisting mainly of the $\alpha\beta$ - and $\gamma\delta$ -acids,

was dissolved in hot carbon disulphide, and, on cooling, crude $\alpha\beta$ -acid separated. From 150 grams of $\beta\gamma$ -acid, 26 grams of crude $\alpha\beta$ -acid were thus obtained, and after some six recrystallisations the acid was quite pure. To obtain the $\gamma\delta$ -acid, the carbon disulphide mother liquor was evaporated to dryness, and the acid transformed into the sparingly soluble calcium salt under the conditions described by Riiber. The acid obtained from the calcium salt still contained $\alpha\beta$ -acid, and this was removed by crystallisation from carbon disulphide and mechanically removing the characteristic plates of the $\gamma\delta$ -acid and crystallising from light petroleum, when 11.5 grams of pure acid, melting at 91° , were obtained.

2. Hydrosorbic acid was prepared as follows. Twenty-five grams of sorbic acid were dissolved in sodium hydroxide solution, and the whole made up to 300 c.c. with water. The solution was transferred to a separating funnel, and placed in a bath at 30 – 35° . Rather more than the theoretical amount of 3 per cent. sodium amalgam was added in small amounts at a time, and the funnel was shaken vigorously after each addition. The reduction proceeded vigorously at the beginning, but slackened toward the end. The mercury was removed, the solution acidified with hydrochloric acid (1:1), and extracted with ether. After removal of the ether, 13 grams of hydrosorbic acid, boiling at $103^\circ/9$ – 10 mm., were obtained. When the distillation was continued, the temperature rose rapidly, but did not become constant.

3. Cinnamylideneacetic and *allocinnamylideneacetic* acids were prepared by Liebermann's method (*Ber.*, 1895, 28, 1441). The *allo*-acid was slightly impure, and melted at 115 – 117° .

4. The β -dimethyl- and trimethyl-acrylic acids were prepared by the methods described previously (*Trans.*, 1909, 95, 977).

We wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has covered part of the cost of this investigation.

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CCLIII.—The Viscosity and Density of Cæsium Nitrate Solutions.

By THOMAS RALPH MERTON, B.Sc. (Oxon).

IN recent years the viscosity of salt solutions has been the subject of numerous investigations, which have mainly been directed toward elucidating the relation between viscosity and electrical conductivity. Most of the alkaline nitrate solutions have been investigated (Grüneisen, *Wiss. Abh. Phys. Tech. Reichsanstalt*, 1904, 4, 239; Applebey, this vol., p. 2000, and others). Very little, however, is known of the viscosity of cæsium salt solutions, with the exception of a single investigation on the viscosity of the chloride solution by Wagner (*Zeitsch. physikal. Chem.*, 1890, 5, 31).

In the present investigation, the viscosities and densities of cæsium nitrate solutions of different concentrations have been determined at 0°, 10°, 18°, and 25°.

EXPERIMENTAL.

The method used for determining viscosity was that of Poiseuille, that is to say, a determination of the times of flow of the solution through a capillary tube. The precautions which must be observed in order to secure an accuracy of one part in a thousand by this method have been thoroughly investigated by Grüneisen (*loc. cit.*, p. 153) and Applebey (*loc. cit.*), whose method I have followed in this investigation, and to whom I am indebted for much valuable assistance in the progress of the work. Two viscometers of the Ostwald type were used.

For viscometers of this type we have:

$$\frac{\eta_{\text{solution}}}{\eta_{\text{water}}} = \frac{(\Delta_{\text{solution}} - d) \times t_{\text{solution}}}{(\Delta_{\text{water}} - d) \times t_{\text{water}}},$$

where η is the viscosity, Δ the density, t the time of flow of the liquid through the capillary, and d the density of air.

Grüneisen (*loc. cit.*) has shown that, for viscometers of the type used, it is unnecessary to apply any correction for the kinetic energy of the liquid in the capillary.

The determination of time offered no difficulty, and was measured by means of a stop-watch reading to one-fifth second, which kept excellent time throughout the investigation.

In order to prove that the flow of the liquids to be investigated in the viscometers obeyed Poiseuille's law, one of the tubes was

calibrated by Gr \ddot{u} neisen's method, with the experimental arrangements used by Applebey (*loc. cit.*). The times of flow of equal volumes of water through the capillary under different hydrostatic pressures are given in the following table:

| Excess pressure (in mm. of water at 15°). | Total pressure. | Time (in 1/5th secs.). | Pressure × time. |
|---|--------------------|---------------------------|---------------------|
| 1.0 | 115.4 | 4573 | 5276 |
| 7.3 | 121.7 | 4338 | 5280 |
| 22.4 | 136.8 | 3865 | 5288 |
| 33.5 | 147.9 | 3566 | 5273 |
| 45.0 | 159.4 | 3298 | 5258 |
| 55.7 | 170.1 | 3091 | 5260 |
| 77.0 | 191.4 | 2755 | 5273 |
| 83.8 | 198.2 | 2663 | 5278 |
| 88.7 | 203.1 | 2585 | 5250 |
| 110.1 | 224.5 | 2340 | 5255 |
| 134.5 | 248.9 | 2115 | 5265 |
| 149.9 | 261.3 | 1990 | 5261 |

As will be seen, the value pressure × time is constant within the limits of experimental error, showing that the flow of liquid through the tube obeys Poiseuille's law, and that the tube can therefore be used for comparative measurements between the limits of time examined.

The second viscometer used in this work was standardised by direct comparison with the first. For this purpose a nearly saturated solution of caesium nitrate has unique advantages, as its high density and low viscosity cause it to flow through the tube more rapidly than water. The ratios of the times of flow of the solution and water in the two tubes were compared, with the following results:

| | Time of flow, water. | Time of flow, solution. | Time of flow of solution, Time of flow of water. |
|---------------------|-------------------------|----------------------------|---|
| Standard tube | 4802 | 4020 | 0.8371 |
| Tube 7 | 4132 | 3459 | 0.8371 |

The constancy of the ratio shows that the second tube obeys Poiseuille's law in exactly the same way as the first.

The viscometers were usually cleaned after use by drawing them through a considerable quantity of the purest available water. If, however, the "water constant" or time of flow of water had changed it was usually re-determined for one of the viscometers after each solution, or if any dust had lodged in the capillary, it was cleaned with a mixture of nitric acid and a drop of alcohol, followed by water. The viscometers were dried by drawing dust-free air through them in a hot-air bath.

In this connexion it may be mentioned that the purity of the air in the room in which the viscometers are dried is of considerable importance. On one occasion there was a certain amount of amyl

acetate vapour in the room in which the viscometers were dried owing to some celluloid varnish containing amyl acetate which had been used there. In consequence of this, anomalous results were obtained, and it was not until the drying apparatus was removed to another room that the viscometers again gave their original water value.

Materials Used.—The cesium nitrate used in this investigation was very kindly lent by the Earl of Berkeley. It was examined spectroscopically, and no trace of any impurity could be found. The water used was the best dust-free water obtainable (the electrical conductivity varied from 1×10^{-6} to 2×10^{-6} mhos.). In making up a solution, the approximate quantity of salt required was placed in a quartz crucible, and heated for about four hours in a quinoline bath at 170° . It was then weighed and dissolved in a known weight of water. The solutions were filtered to remove dust particles.

Determination of Density.—For the determination of density, a pycnometer containing about 12 c.c. of the solution was used. Two settings and two fillings were taken, the pycnometer being weighed against a counterpoise. The pycnometers were "set" in the constant temperature baths in which the viscosity measurements were made. For the densities at 0° , two pycnometers were used, with a small bulb above the capillary to allow for the expansion of the liquid on removing it from the ice, and a glass cap to prevent evaporation. They were set in a jacketed vessel containing crushed ice.

Constant Temperature Baths.—The experiments at 10° , 18° , and 25° were performed in large glass-fronted baths containing about 25 litres of water, vigorous stirring being obtained by means of glass stirrers driven by an electric motor. The temperatures of the baths were verified by means of a standard Goetze thermometer. The 25° bath was heated by a small gas flame, which was governed by a large spiral toluene regulator (Lowry, *Trans.*, 1905, **87**, 142). The 18° bath was heated by a 16 c.p. electric filament lamp placed in a bath close to the stirrer, and governed by a spiral electric regulator.

The 10° bath was identical with that at 18° , except that it contained in addition a coil of metal tubing, through which water was run, to act as a cooling apparatus. No variation in the temperature of these baths could be detected on the thermometer divided in $1/50^\circ$. The 10° bath, with which some trouble was anticipated, was particularly carefully examined with a Beckmann thermometer, but no variation as great as $1/500^\circ$ could be detected.

The experiments at 0° were performed in a large Dewar vacuum vessel, containing crushed ice and water vigorously stirred. At

this temperature rapid stirring was found to be essential in order to prevent accumulation of warmer water at the bottom of the vessel. In the event of a small variation of temperature occurring, a calculated correction can be applied. This correction was found to be about two-fifths second for $1/100^{\circ}$. It is probable that owing to the difficulty of maintaining constant temperature, the results at 0° are not so accurate as at other temperatures.

Density Results.—The results of the density determinations are given in the following tables. As will be seen, the weighings usually agree to within 0.0001, or at most 0.0002, milligram, and therefore the errors in the densities do not exceed 0.00002. Values of $(\Delta - 1) - \text{Concentration} \times \text{Constant}$ are given, from which a sensitive curve can be drawn.

Densities at 0° .

| Parts of cesium nitrate in 100 grams of water. | Mass of solution in pyknometer. | | Mean sp. gr. 1 | Δ_{D} | $(\Delta - 1) - P \times$ 0.0074. |
|---|------------------------------------|---|----------------------|---------------------|--------------------------------------|
| | 1. | 2. | | | |
| 0 | 12.4748 | 14.0425 | | 0.99987 | - 0.00013 |
| 1.0075 | | $\left\{ \begin{array}{l} 14.1507 \\ 14.1507 \\ 14.1507 \end{array} \right\}$ | 1.00770 | 1.00757 | + 0.00010 |
| 1.8784 | | $\left\{ \begin{array}{l} 14.2537 \\ 14.2537 \end{array} \right\}$ | 1.01504 | 1.01491 | + 0.00027 |
| 4.0208 | 13.8832 | 14.4690 | 1.03037 | 1.03023 | + 0.00048 |
| 6.2189 | 14.1033 | 14.6981 | 1.04668 | 1.04654 | + 0.00030 |
| 8.3724 | 14.3110 | 14.9144 | 1.06209 | 1.06195 | + 0.00000 |

Densities at 10° .

| Parts of cesium nitrate in 100 grams of water. | Mass of solution in pyknometer. | Mean sp. gr. | Δ abs. | $(\Delta - 1) - P \times$ 0.0071357. |
|--|---|--------------|---------------|---|
| | | | | |
| 0 | 12.5778 | 1 | 0.99973 | - 0.00027 |
| 1.0167 | $\left\{ \begin{array}{l} 12.6761 \\ 12.6762 \\ 12.6762 \end{array} \right\}$ | 1.00782 | 1.00755 | + 0.00008 |
| 2.1849 | $\left\{ \begin{array}{l} 12.7823 \\ 12.7824 \\ 12.7824 \end{array} \right\}$ | 1.01626 | 1.01598 | + 0.00039 |
| 3.2361 | $\left\{ \begin{array}{l} 12.8800 \\ 12.8801 \\ 12.8801 \end{array} \right\}$ | 1.02403 | 1.02375 | + 0.00066 |
| 5.7336 | $\left\{ \begin{array}{l} 13.1084 \\ 13.1085 \end{array} \right\}$ | 1.04219 | 1.04191 | + 0.00100 |
| 8.8991 | $\left\{ \begin{array}{l} 13.3921 \\ 13.3920 \\ 13.3923 \end{array} \right\}$ | 1.06474 | 1.06445 | + 0.00102 |
| 12.0698 | $\left\{ \begin{array}{l} 13.6741 \\ 13.6742 \\ 13.6741 \end{array} \right\}$ | 1.08716 | 1.08687 | + 0.00075 |
| 14.2910 | $\left\{ \begin{array}{l} 14.7037 \\ 14.7037 \\ 14.7037 \end{array} \right\}$ | 1.10237 | 1.10207 | ± 0 |

Densities at 18°.

| Parts of cesium nitrate in 100 grams of water. | Mass of solution in pycnometer. | | Mean sp. gr. 1 | Δ abs. | $(\Delta - 1) - P$ 0.0079071 - 0.00138 |
|---|------------------------------------|--------------------------------|----------------------|---------------|--|
| | S. | N. | | | |
| 0 | 12.5674 | 8.8160 | | 0.99862 | |
| 1.0060 | { 12.6610 12.6611 12.6610 } | | 1.00745 | | - 0.00090 |
| 2.1415 | { 12.7656 12.7656 12.7656 } | | 1.01577 | 1.01437 | - 0.00063 |
| 3.1209 | { 12.8562 12.8562 12.8562 } | | 1.02208 | 1.02157 | - 0.00096 |
| 5.0677 | { 13.0321 13.0322 13.0322 } | | 1.03698 | 1.03555 | + 0.00004 |
| 6.5582 | | { 9.2372 9.2371 9.2372 } | 1.04778 | 1.04638 | + 0.00017 |
| 9.6569 | | { 9.4290 9.4290 9.4290 } | 1.06958 | 1.06805 | + 0.00053 |
| 12.3740 | { 13.6759 13.6758 13.6759 } | | 1.08820 | 1.08671 | ± 0.00000 |
| 16.6355 | | { 9.8456 9.8456 9.8456 } | 1.11679 | 1.11525 | - 0.00182 |

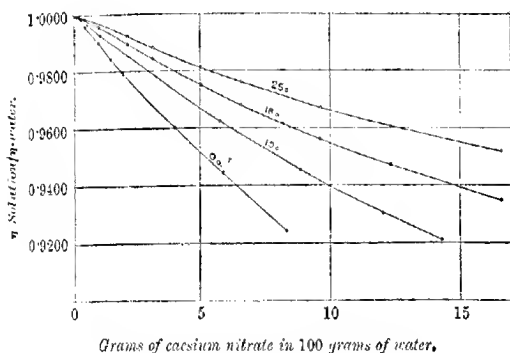
Densities at 25°.

| Parts of cesium nitrate, in 100 grams of water. | Mass of solution in pycnometer. | | Mean sp. gr. 1 | Δ abs. | $(\Delta - 1) - P$ 0.0065215 - 0.00243 |
|--|------------------------------------|--------------------------------|----------------------|---------------|--|
| | S. | N. | | | |
| 0 | 12.5592 | 8.8043 | | 0.99707 | |
| 1.0080 | { 12.6431 12.6431 12.6430 } | | 1.00739 | 1.00443 | - 0.00243 |
| 2.1415 | { 12.7467 12.7465 12.7466 } | | 1.01566 | 1.01263 | - 0.00193 |
| 3.1209 | { 12.8365 12.8365 12.8365 } | | 1.02281 | 1.01981 | - 0.00134 |
| 5.0677 | { 13.0112 13.0111 13.0112 } | | 1.03673 | 1.03360 | - 0.00053 |
| 6.5582 | | { 9.2219 9.2218 9.2219 } | 1.04743 | 1.04436 | - 0.00055 |
| 9.6569 | | { 9.4111 9.4113 9.4114 } | 1.06894 | 1.06580 | - 0.00007 |
| 12.3740 | { 13.6497 13.6496 13.6497 } | | 1.08760 | 1.08441 | - 0.00009 |
| 16.6355 | | { 9.8279 9.8276 9.8279 } | 1.11625 | 1.11298 | - 0.00069 |

Viscosity Results.—The results of the viscosity determinations are given in the following tables. The results are probably correct to ± 2 in 5000 at 18°, 25°, and 10°. At 0° the errors are somewhat greater, but the values given are probably correct to ± 3 in 5000. In Fig. 1 the relative viscosities are plotted against the concentration. Values of $(1-\eta)$ —concentration $\times K$ are given, from which a sensitive curve may be drawn. The viscosity in absolute units has also been calculated, the absolute values of water being taken from Thorpe and Rodger's values (*Phil. Trans.*, 1894, A, 185, 397).

At 0° = 0.01778 At 18° = 0.010510
At 10° = 0.013025 At 25° = 0.00891

FIG. 1.



Discussion of Results.

It will be seen that at all temperatures the viscosity of caesium nitrate solutions is less than that of water. It conforms with the rule found for other salts, in that the decrease of viscosity for unit quantity of salt decreases with increase of concentration. The discovery of Grüneisen (*loc. cit.*), that the viscosity curves of all ionised solutions exhibit a change of curvature at the dilute end, has been confirmed in the case of caesium nitrate. This can be seen in curves in which viscosity is plotted against concentration, but it can be better appreciated by plotting $(1-\eta)/N$ (where N is the normality) against $\sqrt[3]{N}$. In Fig. 2, $1-\eta/N$ is plotted against $\sqrt[3]{N}$ at 18°. It is more convenient to plot $\sqrt[3]{N}$ than N , as in this way the dilute end is more extended. It will be seen that the errors in the determination of $(1-\eta)/N$ increase very rapidly towards the dilute end. For example, in a solution

Viscosities at 0°.

| Parts of casing in 100 parts of water. | Normality (weight) gram-equivalents in 1000 grams of solution. | $\sqrt{\eta}$. | $\Delta \eta$. | Time of flow of solution by viscometer No. | | | | | Mean η (relative). | $1-\eta/N$. | η abs. | $(1-\eta)-P \times$ 0.0093. |
|--|--|-----------------|-----------------|---|--------|--------|--------|---|----------------------------|--------------|-------------|--------------------------------|
| | | | | 5 | 5 | 7 | 7 | 7 | | | | |
| 0.4920 | 0.92518 | 0.9529 | 1.00376 | 0.9623 | 0.9923 | — | — | — | 0.9960 | 0.01301 | 0.017709 | -0.0004 |
| 1.0076 | 0.95120 | 0.9718 | 1.00770 | 0.9826 | 0.9826 | 0.9826 | — | — | 0.9901 | 0.01333 | 0.017703 | +0.0008 |
| 1.5048 | 0.97009 | 0.9838 | 1.01144 | — | — | 0.9729 | 0.9730 | — | 0.9841 | 0.02089 | 0.017497 | +0.0024 |
| 1.9784 | 0.99058 | 0.9984 | 1.01504 | 0.9648 | 0.9648 | 0.9651 | — | — | 0.9793 | 0.02073 | 0.017411 | +0.0028 |
| 4.0208 | 0.9883 | 0.9883 | 1.03037 | 0.9320 | 0.9320 | 0.9318 | 0.9318 | — | 0.9602 | 0.02005 | 0.017383 | +0.0038 |
| 5.9055 | 0.9863 | 0.9863 | 1.04103 | — | 0.9042 | 0.9042 | 0.9044 | — | 0.9441 | 0.01952 | 0.016788 | +0.0026 |
| 8.3724 | 0.9847 | 0.9847 | 1.06209 | 0.8703 | 0.9703 | 0.8703 | — | — | 0.9244 | 0.01908 | 0.016436 | +0.0060 |

Viscosity at 10°.

| Parts of casing in 100 parts of water. | Normality (weight) gram-equivalents in 1000 grams of solution. | $\sqrt{\eta}$. | $\Delta \eta$. | Time of flow of solution by viscometer No. | | | | | Mean η (relative). | $1-\eta/N$. | η abs. | $(1-\eta)-P \times$ 0.005523 |
|--|--|-----------------|-----------------|---|--------|--------|--------|---|----------------------------|--------------|-------------|---------------------------------|
| | | | | 5 | 5 | 7 | 7 | 7 | | | | |
| 0.5728 | 0.9202 | 0.9389 | 1.00427 | 0.9628 | 0.9928 | 0.9928 | — | — | 0.9970 | 0.1027 | 0.019986 | -0.0001 |
| 1.0467 | 0.9582 | 0.9761 | 1.00782 | 0.9857 | 0.9857 | 0.9854 | — | — | 0.9932 | 0.1273 | 0.019835 | -0.0010 |
| 2.2361 | 0.9699 | 0.9839 | 1.02403 | — | — | 0.9557 | 0.9555 | — | 0.9785 | 0.1323 | 0.012746 | +0.0035 |
| 3.7386 | 0.9733 | 0.9859 | 1.04219 | 0.9234 | 0.9234 | 0.9236 | — | — | 0.9625 | 0.1347 | 0.012556 | +0.0059 |
| 5.1190 | 0.9798 | 0.9881 | 1.06474 | 0.8880 | — | 0.8879 | 0.8879 | — | 0.9454 | 0.1393 | 0.012314 | +0.0055 |
| 12.0693 | 0.9527 | 0.9601 | 1.08716 | 0.8563 | 0.8563 | 0.8561 | — | — | 0.9309 | 0.1260 | 0.012245 | +0.0025 |
| 14.3940 | 0.9124 | 0.9224 | 1.10237 | 0.8355 | — | 0.8355 | — | — | 0.9211 | 0.1225 | 0.011937 | -0.0001 |

Isocentres at 18°.

| Parts of caesium nitrate in 100 parts of water. | Normally (weight) gram-equiva- lents in 1000 grams of solution. | \sqrt{N} . | Δ rel. | Time of flow of solution by viscometer No. | | | | Mean η (relative). | $1-\eta/N$. | η abs. | $(1-\eta)-P \times$ 0.004253. |
|--|--|--------------|---------------|---|---|--------|--------|----------------------------|--------------|-------------|----------------------------------|
| | | | | 5 | 7 | 5 | 7 | | | | |
| 0.4529 | 0.02414 | 0.2350 | 1.00333 | 0.9852 | — | 0.9954 | 0.9954 | 0.9986 | 0.06050 | 0.010435 | -0.0005 |
| 1.0060 | 0.0511 | 0.3711 | 1.00745 | 0.9885 | — | 0.9886 | 0.9886 | 0.9960 | 0.07527 | 0.010468 | -0.0003 |
| 2.1416 | 0.1076 | 0.4757 | 1.01577 | 0.9746 | — | 0.9746 | — | 0.9960 | 0.07527 | 0.010468 | +0.0009 |
| 3.1269 | 0.1557 | 0.5380 | 1.02268 | 0.9623 | — | 0.9622 | — | 0.9814 | 0.07527 | 0.010468 | +0.0022 |
| 5.0677 | 0.2475 | 0.6278 | 1.03698 | 0.9403 | — | 0.9404 | — | 0.9752 | 0.10019 | 0.010316 | +0.0031 |
| 6.5882 | 0.3178 | 0.820 | 1.04778 | 0.9238 | — | 0.9238 | — | 0.9681 | 0.10020 | 0.010219 | +0.0037 |
| 9.6568 | 0.4530 | 0.7674 | 1.05653 | 0.8940 | — | 0.8940 | — | 0.9561 | 0.10058 | 0.010175 | +0.0025 |
| 12.3740 | 0.5652 | 0.8269 | 1.06821 | 0.8792 | — | 0.8792 | — | 0.9479 | 0.09712 | 0.010049 | +0.0025 |
| 16.9355 | 0.7321 | 0.9016 | 1.11679 | 0.8371 | — | 0.8371 | — | 0.9347 | 0.08377 | 0.009853 | 0.0 |
| | | | | | | | | 0.9347 | 0.08382 | 0.009336 | -0.0071 |

Viscosity at 25°.

| Parts of caesium nitrate in 100 parts of water. | Normally (weight) gram-equiva- lents in 1000 grams of solution. | \sqrt{N} . | Δ rel. | 5 | 7 | 5 | 7 | Mean η (relative). | $1-\eta/N$. | η abs. | $(1-\eta)-P \times$ 0.0032. |
|--|--|--------------|---------------|--------|---|--------|---|----------------------------|--------------|-------------|--------------------------------|
| | | | | | | | | | | | |
| 0.4529 | 0.02414 | 0.2350 | 1.00333 | 0.9856 | — | 0.9954 | — | 0.9986 | 0.06050 | 0.010435 | -0.0005 |
| 1.0060 | 0.0511 | 0.3711 | 1.00745 | 0.9885 | — | 0.9886 | — | 0.9960 | 0.07527 | 0.010468 | -0.0003 |
| 2.1416 | 0.1076 | 0.4757 | 1.01577 | 0.9746 | — | 0.9746 | — | 0.9960 | 0.07527 | 0.010468 | +0.0009 |
| 3.1269 | 0.1557 | 0.5380 | 1.02268 | 0.9623 | — | 0.9622 | — | 0.9814 | 0.07527 | 0.010468 | +0.0022 |
| 5.0677 | 0.2475 | 0.6278 | 1.03698 | 0.9403 | — | 0.9404 | — | 0.9752 | 0.10019 | 0.010316 | +0.0031 |
| 6.5882 | 0.3178 | 0.820 | 1.04778 | 0.9238 | — | 0.9238 | — | 0.9681 | 0.10020 | 0.010219 | +0.0037 |
| 9.6568 | 0.4530 | 0.7674 | 1.05653 | 0.8940 | — | 0.8940 | — | 0.9561 | 0.10058 | 0.010175 | +0.0025 |
| 12.3740 | 0.5652 | 0.8269 | 1.06821 | 0.8792 | — | 0.8792 | — | 0.9479 | 0.09712 | 0.010049 | +0.0025 |
| 16.9355 | 0.7321 | 0.9016 | 1.11625 | 0.8371 | — | 0.8371 | — | 0.9347 | 0.08377 | 0.009853 | 0.0 |
| | | | | | | | | 0.9347 | 0.08382 | 0.009336 | -0.0071 |

with a relative viscosity of 0.9980, $(1-\eta)$ would be 0.0020, so that an error of 0.01 per cent. would produce an error of about 4 per cent. in the value of $1-\eta/N$, whereas if the viscosity were 0.9999, a similar error would alter $1-\eta/N$ by less than 0.125 per cent.

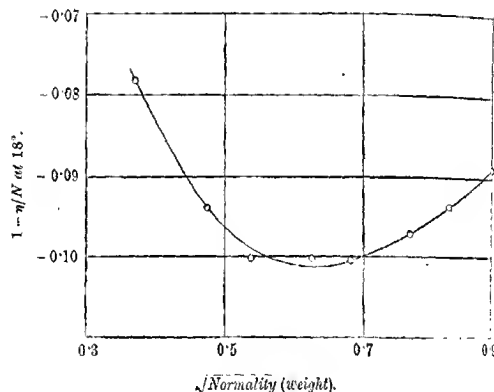
It would be of great interest to discover, if possible, the value of $1-\eta/N$ for infinite dilution, but, as has been shown, the errors increase so rapidly towards the dilute end that it becomes impossible to form any estimate.

Grüneisen (*loc. cit.*) has proposed the formula:

$$\eta - 1/N = Ai + B(1-i) + CN,$$

where i is the ratio L/L_0 , L and L_0 being the molecular electric conductivities at concentrations N and 0, and A , B , and C at

FIG. 2.



constants depending on the nature of the salt. Grüneisen has obtained fairly good agreement in his results between the found values of η and those calculated by this formula. I have not been able to find any determinations of the electrical conductivity of caesium nitrate solutions, and have therefore been unable to make any attempt to apply the formula to my results.

From the absolute values calculated from Thorpe and Rodgers (*loc. cit.*) values for water, it will be seen that the change of viscosity produced by a rise in temperature decreases with increasing concentration. Thus, 7 parts of caesium nitrate in 100 parts of water lower the viscosity about 7.5 per cent. at 0°, but less than 3 per cent. at 25°.

The general form of the viscosity curve is precisely what we

should expect from the position of caesium in the periodic system, a comparison with the viscosities of lithium, sodium, and potassium nitrates, taken from Grüneisen's paper, showing that, qualitatively, the viscosity changes follow the classification of the elements in the periodic system. If we may assume that the viscosity of a solution depends on the mean size of the molecules and ions, we should infer that of the alkali metals the caesium ion is the smallest, in aqueous solution, that is to say, it has a smaller number of water molecules attached to it than the ions of the other alkali metals. In agreement with this, the caesium ion is known to possess the largest ionic mobility.

Summary.

The viscosities of caesium nitrate solutions have been investigated at 0°, 10°, 18°, and 25°. The results confirm in every respect the general principles discovered for other salt solutions.

The densities of the solutions at these temperatures have been determined. In these determinations, no abnormal results have been found. The change of density per unit quantity of salt decreases slightly with an increase of concentration.

The effect of temperature on the viscosity has been examined, and found to decrease with increasing concentration.

With respect to the viscosity of the nitrate solutions, caesium occupies a position among the alkalis in accordance with its position in the periodic system.

In conclusion, I should like to express my thanks to Mr. H. B. Artley and Mr. D. H. Nagel for the kind assistance and advice they have given me in this investigation.

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CLIV.—The Homogeneous Decomposition of Ozone in the Presence of Oxygen and Other Gases.

By DAVID LEONARD CHAPMAN and HERBERT EDWIN JONES.

It has been shown by H. E. Clarke and one of us (Trans., 1908, 3, 1638) that the rate of decomposition of ozone on the surface of glass is so slow that even in moderately small globes the amount of ozone destroyed on the internal surface of the vessel may be neglected in comparison with that decomposed in the interior of

the gas. In other words, it has been demonstrated that the conversion of ozone into oxygen under suitable conditions may be assumed to be a homogeneous change without any appreciable error being made. It is the only slow chemical change in the gaseous state which has, as yet, been shown to satisfy the condition of homogeneity under realisable conditions.

Since the quantitative investigation of a chemical change entirely confined to matter in its least complex state might be expected to furnish results of exceptional theoretical significance, an attempt was made by Mr. H. E. Clarke and one of us to construct an apparatus with which the velocity of decomposition of ozone in the presence of oxygen and other gases might be measured; but before the apparatus had been sufficiently perfected to furnish satisfactory results, Mr. Clarke was unfortunately compelled to relinquish the work. The investigation has been continued by the authors of this communication with the aid of a slightly modified and improved form of the apparatus originally designed by Clarke and one of us. Before giving a detailed account of this apparatus, and the mode of conducting an experiment, it will be convenient to state the general conclusions that have been drawn from the results, and to indicate what we believe to be the theoretical significance of these conclusions.

The results demonstrate that:

(a) Oxygen, nitrogen, carbon dioxide, and possibly water vapour have no effect on the rate of decomposition of ozone, that is, the rate of decomposition of ozone in the presence of these gases is a function of the concentration of the ozone only.

(b) Nitrogen peroxide (Andrews) and chlorine accelerate in a marked degree the decomposition of the gas.

(c) If the order of the change can be represented exactly by an integral ordinal number, that number is the second.

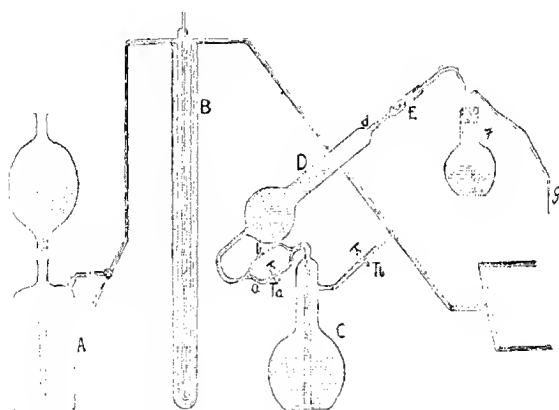
In respect of their influence on the rate of decomposition of ozone, gases may therefore be separated into two classes—those which are without effect, and those which act as powerful catalysts. That a classification based on such a striking distinction should be possible lends strong support to the view that the catalytic action of the second class is chemical rather than physical in its nature, since a physical property is generally shared, in a greater or less degree, by all gases. Moreover, nitrogen peroxide and chlorine are substances of which the first is known to react with ozone, and the second is closely related to an element, namely, iodine, which has been shown to be oxidised by ozone.

The facts, so far as they have been made out, indicate that the mechanism of the decomposition of ozone in the absence of catalysts

is a simple process, consisting of the conversion of two molecules of ozone during a favourable collision into three molecules of oxygen. Such a view is in harmony with the fact that gases having no chemical action on ozone are without influence on its rate of decomposition (for the number of collisions between pairs of molecules of ozone is almost independent of the diluting gas), and also with the fact that the reaction is of the second order.

A result of exceptional interest is that which relates to the

FIG. 1.



influence of moisture. The discussion of this will be relegated to the experimental section of the paper.

EXPERIMENTAL.

The apparatus used for the preparation and collection of the ozonised oxygen is depicted in Fig. 1. The oxygen was prepared by heating potassium permanganate. Dust and carbon dioxide were removed from it by its being passed through a tube packed with glass wool and soda-lime. It was stored in a small gas-holder A, which contained concentrated sulphuric acid. The gas-holder was connected by narrow capillary tubing with a Brodie ozone generator B, made of thin glass, as recommended by Shenstone (*Trans.*, 1893, **63**, 938). The generator was immersed in dilute sulphuric acid, and its inner tube contained metallic mercury. It was connected by capillary tubing with a vessel C, containing concentrated sulphuric acid saturated with ozone. As the ozonised oxygen passed into this vessel, the displaced acid entered the

reservoir *D*. The receptacles *D* and *C* were connected by a wide tube *a*, in which a tap *T_a* was inserted, and also by a tube *b* of very fine bore.

When *T_a* was closed, the acid entered *D* very slowly, owing to the resistance offered to its motion by the capillary tube, and the rate at which the ozonised oxygen entered the receiver was correspondingly slow. The upper end of *D* was connected with a device by means of which the current of gas could be further regulated. The wide tube *E*, containing powdered potassium hydroxide, was ground into the mouth *d* of the receptacle *D*. *E* was in turn joined by rubber tubing to a flask *F*, containing water, which could be siphoned out drop by drop through the fine capillary tube *G*. By raising and lowering *G*, the rate at which the water siphoned over could be regulated, and the flow of gas through the ozone generator thereby controlled. The potassium hydroxide in *E* served to destroy traces of ozone which would otherwise have attacked the rubber tube. Before use, the apparatus was cleansed with a hot mixture of potassium chromate and concentrated sulphuric acid, and then with hot distilled water, and thoroughly dried.

All air was displaced from the apparatus before starting an experiment by a current of oxygen. Oxygen was collected in the gas-holder, and a volume of ozonised oxygen sufficient for one experiment was prepared from it. The tap *T_b* was then closed, and the oxygen remaining in the gas-holder *A* was allowed to escape. The gas in the receiver *C* was next transferred to the holder *A*, the taps *T_a* and *T_b* being left open. It was then again drawn slowly through the ozone generator into the receiver *C*, the coil being in action. The percentage of ozone was appreciably increased by the gas being submitted for a second time to the action of the silent discharge.

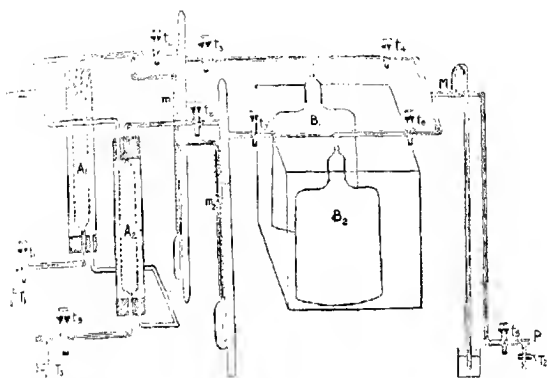
The section of the apparatus used to measure the rate of decomposition of the ozone (at 100°) is shown in Fig. 2.

The glass tubes, *A₁* and *A₂*, of about 100 c.c. capacity, in which the ozone was heated, communicated by capillary tubes, on the one side with the previously described section of the apparatus, and on the other with the left-hand limbs of the manometers *m₁* and *m₂*, which contained concentrated sulphuric acid. The right-hand limbs of the manometers were connected by capillary tubes and ground glass joints with two bottles, *B₁* and *B₂*, of about 2 litres capacity each. The corresponding parts of the apparatus were made as nearly alike as possible. The apparatus was connected with an injector pump at *P*, and was provided with a mercury manometer at *M*, as shown in the diagram. Taps *T₁*, *T₂*, and *T₃*, and taps *t₁*, *t₂*, *t₃*, *t₄*, *t₅*, *t₆*, *t₇*, *t₈*, and *t₉*, provided with mercury seals, were

inserted in the positions indicated in the figure. The pressure on the right-hand side of the manometers was kept constant by the bottles being immersed in a bath of water at a fixed temperature. The water in the bath was stirred by a current of air, and the temperature was controlled by a delicate electric thermoregulator.

During an experiment the tubes A_1 and A_2 were kept at 100° by means of a current of steam, which entered the jackets surrounding them from above. In a preliminary experiment, it was shown that the temperature of both of the tubes could be raised to that of the steam in the same time. Before the experiments

FIG. 2.



were started, ozonised oxygen was passed through the heated tubes for several hours.

Influence of Oxygen on the Rate of Decomposition of Ozone.

The object of the first series of experiments was to ascertain the effect, if any, of varying concentrations of oxygen on the rate of decomposition of the ozone. The method of conducting an experiment was as follows.

A quantity of ozonised oxygen sufficient for one experiment was collected in C , the ozone remaining in the generator and capillary tubes being subsequently driven out through the taps T_1 and T_3 by a stream of oxygen from the holder A .

With the taps t_1 , t_9 , and T_2 closed, and t_2 , t_3 , t_4 , t_5 , t_6 , t_7 , and t_8 open, the apparatus was exhausted as completely as possible by the injector pump. The taps t_6 , t_3 , and t_7 were then closed, and oxygen

admitted from the holder A through t_1 and t_2 until the volume between the taps t_1 and t_3 and between the taps t_2 and t_4 had been filled. The pump was again set in action, and the taps t_3 , t_4 , and t_7 cautiously opened. When the limit of exhaustion attainable with the injector pump had been reached, the process described above was repeated, the removal of traces of air from the tubes A_1 and A_2 being thereby ensured.

After the final exhaustion the taps t_5 , t_2 , and t_8 were closed. By cautiously opening t_1 and t_6 , ozonised oxygen was admitted to the tubes A_1 and A_2 from the receiver C , the pressure on both sides of the manometer being maintained the same by the simultaneous admission of air into the bottles B_1 and B_2 through the taps t_3 and T_2 . When the manometer M indicated a pressure of a little less than half an atmosphere, t_4 was closed. The ozone left in the capillary tubes on the left-hand side of the taps t_1 and t_6 was displaced by oxygen, and oxygen was then introduced into the tube A_2 by carefully opening the tap t_9 , air being at the same time admitted through t_5 . The taps t_6 and t_9 were closed when the manometer m indicated a pressure slightly less than an atmosphere.

The tube A_1 was thus filled with ozonised oxygen at the pressure of half an atmosphere, whilst A_2 contained the same amount of ozone, but approximately twice as much oxygen.

The tubes having been filled, the taps t_2 and t_8 were opened, and a rapid current of steam was passed through the steam jackets. After one and a-half minutes (when the contents of the tubes had attained the temperature of the steam), the taps t_2 and t_8 were closed. The differences of pressure registered by the manometers were noted at regular intervals. Curves were plotted, showing the relation between the increase of pressure in the tubes A_1 and A_2 and the time. It sometimes happened that the total amounts of ozone contained in A_1 and A_2 respectively (as indicated by the total change of pressure) were not exactly equal. In such cases a simple correction was applied in order that the results might be strictly comparable.

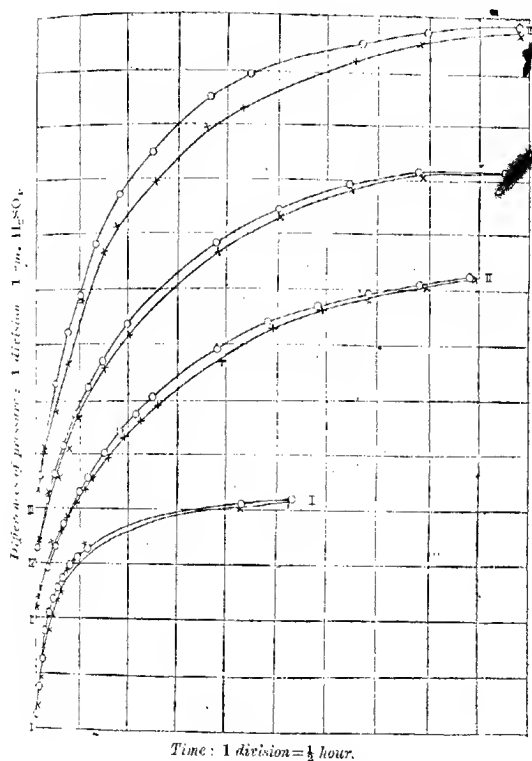
The changes of pressure in cm. of sulphuric acid are plotted against the times, and the four pairs of curves thus obtained are shown in Fig. 3. The circles correspond to the changes of pressure in the tube which contained ozonised oxygen at a pressure of half an atmosphere, and the crosses to changes of pressure in the other tube which contained the same amount of ozone per unit volume, but twice as much oxygen. The numbers attached to the curves indicate the order in which the experiments were performed.

These results point decisively to the conclusion that variation in

the pressure of the oxygen mixed with ozone is unattended by appreciable alteration in the velocity of decomposition of the latter gas at 100° . This conclusion does not appear to agree with the observations of previous investigators.

S. Jahn (*Zeitsch. anorg. Chem.*, 1906, **48**, 260) and Perman and

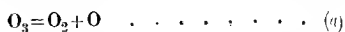
FIG. 3.



Greaves (*Proc. Roy. Soc.*, 1908, *A*, **80**, 353) assert that the rate of decomposition of ozone varies approximately inversely as the oxygen-pressure. If the reaction were reversible, this result might be expected; but Perman and Greaves and others have conclusively demonstrated that at 100° it may be regarded as irreversible.*

* Fischer and Braehmer (*Ber.*, 1906, **39**, 940), have recently shown that ozone is formed in small quantities from oxygen at temperatures above 1300° .

In order to explain his results, Jahn has suggested that the decomposition of ozone occurs in two stages, expressible by the equations:



the first stage being rapid and reversible, whilst the second is slow. These assumptions would require that the rate of decomposition of the ozone should be directly proportional to the square of the concentration of the ozone, and inversely proportional to the concentration of the oxygen. Jahn's experiments were carried out at 127°, at which temperature the reaction is bimolecular, according to Warburg (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, **48**, 1126).

Perman and Greaves, on the other hand, consider that Jahn's hypothesis is not justifiable, and that the alleged effect of the oxygen is due to variations in the gas film on the glass surface resulting from the changes in the oxygen-pressure. If, however, the decomposition occurs mainly in the body of the gas, as appears from the work of Clarke and one of us (*loc. cit.*), the suggestion must for that reason alone be discarded.

Influence of Aqueous Vapour on the Rate of Decomposition of Ozone.

A second series of experiments was performed in order to investigate the influence of water vapour on the rate of decomposition of the gas—a subject of considerable interest, both on account of the diversity of the results obtained by previous workers and of its bearing on the general problem of the catalytic effect of moisture on most simple chemical changes.

The experiments were carried out as described above, except that both tubes were filled with ozonised oxygen at a pressure of a little less than an atmosphere, and that the gas which entered the tube A_1 was saturated with water vapour by its being passed through a small wash-bottle containing distilled water. To prevent any moisture being carried over into A_2 , a tap was inserted on the left-hand side of the wash-bottle, which was shut off while A_2 was being filled.

The eight curves obtained by plotting the results of four experiments are shown in Fig. 4. In experiments IIIa and IVa, the moist gas was contained in the tube which held the dry gas in the two previous experiments. The crosses correspond to the changes of pressure of the moist gas, and the circles to the changes of pressure of the gas dried by concentrated sulphuric acid.

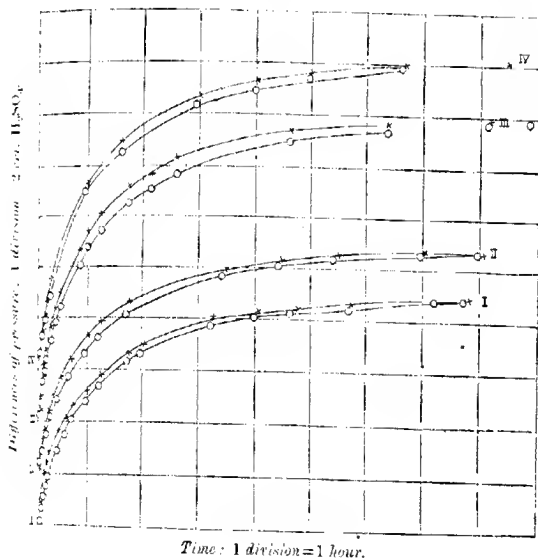
Andrews and Tait, and also Brodie, in their classical memoirs on

ozone, recommend the use of carefully dried oxygen for the preparation of ozone by the silent discharge.

Shenstone and Cundall (*Trans.*, 1887, 51, 610) showed that carefully dried oxygen can be easily converted into ozone—a fact which was shortly afterwards confirmed by Baker (*Trans.*, 1894, 65, 611), who stated that “ozone was formed as rapidly in oxygen dried with phosphorus pentoxide as it was in the same tube when the oxygen had been dried only by sulphuric acid.”

As a result of further investigations, Shenstone (*Trans.*, 1897, 71, 471) drew the remarkable conclusion that all previous state-

FIG. 4.



ments on the subject were wrong. He observed that a high percentage of ozone is formed by the action of the silent discharge on oxygen saturated with water vapour, and that the ozone thus produced is remarkably stable. On partly drying the gas, the percentage of ozone produced was considerably reduced, and the gas was found to be singularly unstable. Oxygen which had been thoroughly dried was found to become ozonised exceedingly badly. Subsequent investigations have failed to confirm Shenstone's work, and Armstrong has suggested that his anomalous results may be due to the presence of oxides of nitrogen (formed by continuous action of

the discharge from traces of nitrogen contained in the oxygen), which, as Andrews has shown, immediately destroy ozone.

Thomson and Threlfall (*Proc. Roy. Soc.*, 1885, **40**, 340) assert that ozone is produced when an electric spark is passed through very carefully dried oxygen.

Warburg (*loc. cit.*) maintains that at 100° the dry gas is just as stable as the moist.

Warburg and Leithäuser (*Ann. Physik*, 1906, [iv], **20**, 751) have, moreover, shown that the formation of ozone both in oxygen and in air is retarded by the presence of moisture, the retardation being greater in oxygen than in air.

Fischer and Marx (*Ber.*, 1906, **29**, 3631), working with a Nernst filament, find that the first traces of moisture lessen the yield of ozone by catalytic action, whereas larger quantities of water vapour increase the yield of hydrogen peroxide at the expense of the ozone.

Perman and Greaves (*loc. cit.*) claim to have shown that water vapour accelerates the decomposition of ozone, and that the effect is roughly proportional to the amount of water vapour present. They consider that the effect is due to the deposition of moisture on the surface of the glass, which causes the ozone to be more rapidly condensed. They point out that their results do not agree with those of Shenstone.

Although in our experiments the ozone mixed with a considerable proportion of water vapour appears to decompose at a slightly greater rate than that which has been dried with sulphuric acid, the difference is so small that we are disposed to think that it ought to be attributed to the gradual removal of water vapour, adsorbed on the inner surface of the glass, at the higher temperature, or to some similar cause. We are, at least, justified in concluding that at 100° a large difference in the quantity of water vapour present with the ozone is not accompanied by any marked change in the velocity of decomposition. Our results agree with those of Warburg, whose experiments were also conducted at 100°.

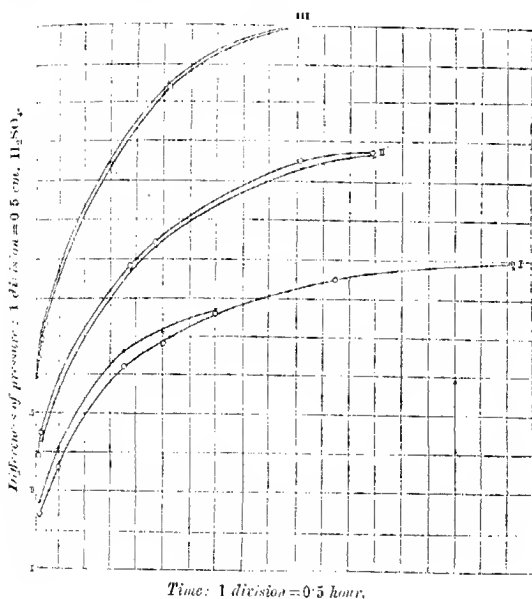
Influence of Nitrogen, Carbon Dioxide, Carbon Monoxide, and Chlorine on the Rate of Decomposition of Ozone.

The negative character of the results obtained with the first three gases is sufficient proof that no appreciable quantity of impurity capable of destroying the ozone was contained in them. In each case concentrated sulphuric acid was used to dry the gas. The experiments were conducted as follows.

A tube containing soda-lime was introduced between the gas-holder and the ozone generator in order to remove any carbon dioxide from the oxygen. The tubes A_1 and A_2 were filled with

ozonised oxygen at a pressure of half an atmosphere in the manner previously described. Oxygen was then admitted to one tube until a pressure slightly less than an atmosphere was registered by the manometer. The gas of which the effect was being investigated was then introduced into the other tube through T_1 or T_3 until the pressure in both tubes was the same. The rates of decomposition of the ozone in the two tubes were compared. Several experiments were performed, the gas under investigation being introduced into A_1 and A_2 alternately.

FIG. 5.



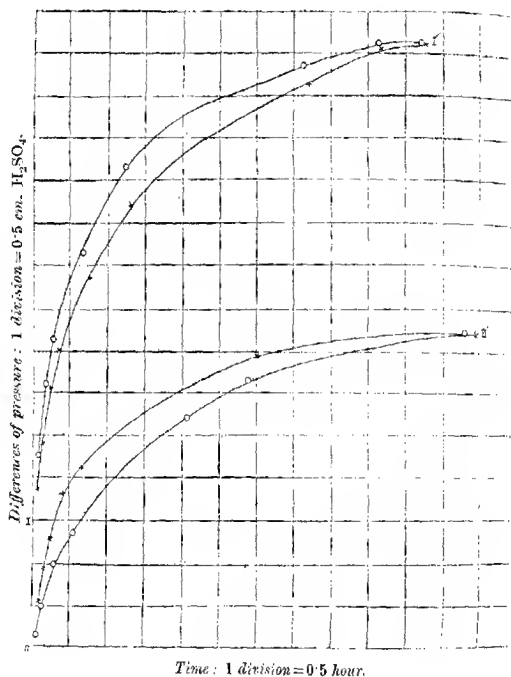
In the case of nitrogen, no effect on the velocity of decomposition was observed, while the experiments with carbon dioxide and carbon monoxide demonstrate that the influence, if any, of these gases is small. Chlorine, on the other hand, was found to decompose ozone so rapidly that it was quite impossible to make any trustworthy measurement of the velocity of decomposition.

The six curves obtained by plotting the results of three experiments with nitrogen are shown in Fig. 5. In the experiments II and III, the nitrogen was contained in the tube which in the previous experiment held ozonised oxygen only. The crosses

correspond to changes of pressure in the gas which contained nitrogen, and the circles to the changes of pressure in the other tube.

The readings taken in the experiments with carbon dioxide I and carbon monoxide II are plotted in the curves shown in Fig. 6. The circles correspond to changes of pressure in the tube which contained the ozonised oxygen only.

FIG. 6.



Shenstone and Evans (*Trans.*, 1898, **73**, 246), while investigating the influence of the silent discharge on atmospheric air, were surprised to find that as much as 98 per cent. of the oxygen contained in the air could be converted into ozone, the maximum yield of ozone obtained from pure oxygen under the same conditions being only 13.6 per cent. A similar observation was made by Brodie (*Phil. Trans.*, 1874, **164**, 101) when he submitted carbon

dioxide to the action of the same agency; the carbon dioxide was decomposed into carbon monoxide and oxygen, 85 per cent. of the oxygen being in the form of ozone. It was conceivable that these interesting and peculiar phenomena might arise from inhibitive effects on the thermal decomposition of ozone of nitrogen and carbon dioxide respectively. The above experiments demonstrate that such an explanation is untenable, and that the phenomena in question must be due to some obscure influence of the nitrogen on the one hand, and the carbon dioxide or carbon monoxide on the other, on the energy of the discharge itself.

Observations on the Order of the Change.

In examining our results with a view to determining the order of the change, we have adopted a novel method. Instead of calculating the value of the constant for each observation on the assumption that the change is of a given order, we compare the amounts of ozone decomposed at given intervals of time with those calculated for changes of a specified order. This method of examining the results has the obvious advantage of enabling us to decide at a glance whether the departure of the experimental numbers from those calculated from any given set of assumptions as to the nature of the change lie within the limits of experimental error.

A curve of a given order is drawn through three points on the experimental curves, the points selected being the origin, and the points corresponding with the last observation, and an observation made when about half of the ozone was decomposed. The difference between the magnitudes of ordinates (amounts of ozone) of the experimental and calculated curve at different times are then tabulated. In the present case it was only necessary to compare the experimental curve with calculated curves drawn through it of the first and second order. It will be seen from the numbers given that the reaction is very nearly of the second order. Only the numbers obtained in those experiments in which large quantities of dry ozone were decomposed, and in which readings were taken for a considerable period of time are submitted to examination below.

Examination of the Measurements Made in Experiment IIa. (1.)

| Time. | Observed change of pressure. | Calculated change of pressure, 1st order. | Difference: $k_1=0.00648$. | Observed change of pressure. | Calculated change of pressure, 2nd order. | Difference: $k_2=9.96/12$. |
|----------------------------|------------------------------------|--|--------------------------------|------------------------------------|--|--------------------------------|
| 2 | 0.60 | 0.38 | +0.24 | 0.60 | 0.48 | +0.12 |
| 5 | 1.30 | 0.91 | +0.39 | 1.30 | 1.16 | +0.14 |
| 10 | 1.90 | 1.68 | +0.22 | 1.90 | 2.13 | -0.23 |
| 16 | 2.95 | 2.57 | +0.38 | 2.95 | 3.11 | -0.16 |
| 58 | 7.00 | 7.00 | 0 | 7.00 | 7.00 | 0 |
| 97 | 8.50 | 9.26 | +0.71 | 8.50 | 8.65 | +0.10 |
| 178 | 10.30 | 11.26 | +0.96 | 10.30 | 10.07 | -0.23 |
| 238 | 10.95 | 11.76 | +0.81 | 10.95 | 10.93 | -0.02 |
| 298 | 11.40 | 11.97 | +0.57 | 11.40 | 11.34 | -0.06 |
| 397 | 11.85 | 12.08 | +0.23 | 11.85 | 11.78 | -0.07 |
| 508 | 12.10 | 12.10 | 0 | 12.10 | 12.10 | 0 |
| Sum of differences = +4.51 | | | | Sum of differences = -0.11 | | |

The calculated curves are drawn through the origin, the point (58, 7.00), and the point (508, 12.10). If the difference between the ordinates of the calculated and experimental curves indicates that the order of the reaction is of a higher value than that corresponding with the calculated curve, a plus sign is attached to it, a minus sign having the reverse significance.

It will be evident on inspection of the above numbers that the reaction differs but slightly from one of the second order.

Examination of the Measurements made in Experiment IIIa. (1.)

In this experiment the rate of change approximates still more closely to a reaction of the second order.

| Time. | Observed change of pressure. | Calculated change of pressure, 1st order. | Difference: $k_1=0.00624$. | Observed change of pressure. | Calculated change of pressure, 2nd order. | Difference: $k_2=0.00141$. |
|----------------------------|------------------------------------|--|--------------------------------|------------------------------------|--|--------------------------------|
| 1 | 0.25 | 0.17 | +0.08 | 0.25 | 0.23 | +0.02 |
| 3 | 0.75 | 0.50 | +0.25 | 0.75 | 0.69 | +0.06 |
| 6 | 1.55 | 0.95 | +0.60 | 1.55 | 1.30 | +0.25 |
| 9 | 1.95 | 1.44 | +0.51 | 1.95 | 1.86 | +0.09 |
| 12 | 2.40 | 1.88 | +0.52 | 2.40 | 2.36 | +0.04 |
| 18 | 3.15 | 2.69 | +0.46 | 3.15 | 3.25 | -0.10 |
| 24 | 3.85 | 3.26 | +0.59 | 3.85 | 4.00 | -0.15 |
| 30 | 4.50 | 4.15 | +0.35 | 4.50 | 4.64 | -0.14 |
| 51 | 6.10 | 6.16 | -0.06 | 6.10 | 6.35 | -0.25 |
| 60 | 6.85 | 6.85 | 0.00 | 6.85 | 6.85 | 0.00 |
| 75 | 7.50 | 7.82 | +0.32 | 7.50 | 7.60 | +0.10 |
| 105 | 8.60 | 9.24 | +0.64 | 8.60 | 8.61 | +0.01 |
| 129 | 9.15 | 10.00 | +0.85 | 9.15 | 9.19 | +0.04 |
| 156 | 9.75 | 10.60 | +0.85 | 9.75 | 9.69 | -0.06 |
| 276 | 11.00 | 11.63 | +0.63 | 11.00 | 10.92 | -0.08 |
| 381 | 11.40 | 11.81 | +0.41 | 11.40 | 11.43 | +0.03 |
| 489 | 11.80 | 11.85 | +0.05 | 11.80 | 11.76 | -0.04 |
| 531 | 11.85 | 11.85 | 0.00 | 11.85 | 11.85 | 0.00 |
| Sum of differences = +7.06 | | | | Sum of differences = -0.18 | | |

In the other experiments, in which the initial percentage of ozone was less, or the period during which observations were made shorter, the order of the change falls to a greater extent below the second. All the experiments are conclusive in demonstrating, however, that if the order of the change can be represented by an integral ordinal number, that number is the second.

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CLV.—*The Colour Changes of Methyl-Orange and Methyl-Red in Acid Solution.*

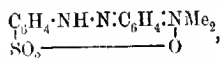
By HENRY THOMAS TIZARD.

It is well known that the colour of an indicator in solution depends, within certain limits, on the concentration of the hydrogen ion (or hydroxyl ion) in the solution. These limits, which vary greatly with the nature of the indicator, have been determined for a large number of indicators by Fels (*Zeitsch. Elektrochem.*, 1904, **10**, 208) and Salessky (*ibid.*, p. 205), and a knowledge of them enables us to choose, for any given volumetric operation, the indicator that will give the best results. Conversely, by testing a solution with a large number of indicators, we can arrive at an estimate of the concentration of hydrogen ions in it. Friedenthal (*Zeitsch. Elektrochem.*, 1904, **10**, 114) and Salm (*Zeitsch. physikal. Chem.*, 1906, **57**, 471) have measured in this way the degree of dissociation of weak acids and weak bases, and have obtained results agreeing often to within a few per cent. of those obtained by conductivity measurements; but it can hardly be seriously proposed to supersede the latter, more accurate, although more laborious, method by the former, except when the acid or base under investigation is extremely weak. On the other hand, the determination of the degree of hydrolysis of salts in aqueous solution is often both laborious and at the same time subject to large percentage errors; a simple colorimetric method would therefore be of considerable importance, provided that it could be made as accurate as, or more so than, the methods usually employed. Friedenthal's method cannot be considered accurate enough for this purpose; the difficulty of judging colours without employing a suitable apparatus is very great, and, moreover, it is impossible to keep weakly acidic standard solutions of indicators (for comparison) unchanged for any length of time. It is far better to determine once and for all the relation between depth of colour and the concentration of the hydrogen ion.

For this purpose only those indicators can be used that are either colourless in one form, or exist in two coloured forms which are practically alike in tint and only differ in depth of colour. For all practical purposes, methyl-orange sufficiently fulfils the latter condition; the complete change of colour of this indicator from alkaline to strongly acid solutions can be followed by matching it against a suitable standard solution in a tintometer. I have therefore examined this change of colour with as great care and accuracy as possible, and have applied the results obtained to the determination of the hydrolysis of aniline salts at different dilutions (see following paper). Velcy, in a series of papers (*Zeitsch. physikal. Chem.*, 1906, 57. 147; *Trans.*, 1907, and following years), has to a large extent opened up the field in this direction; but he worked only with extremely dilute solutions, where the total colour change is small, and the error of observation relatively large. Further, he based all his conclusions on empirical relations, which can be only approximately true. For these and other reasons, which will be mentioned later, his results can only be considered qualitative.

Theory of the Colour Change.

The simplest theory of the colour changes of an indicator is that of Ostwald. According to this, the ions of an indicator have a different colour from that of the undissociated molecule. For example, the undissociated molecule, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ is red, whilst the ion, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3'$, is light yellow. It has recently been proved in many cases, and is probably true in all, that this change in ionisation is accompanied by a change in the chemical structure of the molecule. According to Hewitt, the undissociated molecule of methyl-orange mainly consists of an internal compound,



to which the deep red colour is due. From this point of view, indicators are pseudo-acids, the pseudo-acidic form being always in equilibrium with the true acidic form, from which the ions are directly derived. It must, however, be emphasised that these considerations make no difference whatever to the theoretical treatment from the ionic point of view; for if the undissociated acid exists in solution in two or even more forms, these must always be present in strictly constant ratios, and hence, for all practical purposes, the acid behaves as if it existed in only one form. This will be assumed to be true for the sake of clearness in the following considerations, but it must be understood that the results obtained have no bearing

in the question as to what particular form of the undissociated molecule the deep red colour is due.

Now let the molecular colour of the ion be taken as unity, and let that of the undissociated acid be equal to c_1 . By this we mean that if the colour of a solution containing completely dissociated methyl-orange is balanced by a height " h " of a standard solution in a tintometer, the colour of the same solution when excess of acid (hydrochloric) is added, that is, when the indicator is entirely in the undissociated form, will be balanced by a height $= c_1 \times h$. Then the molecular colour of a solution containing methyl-orange partly in the undissociated form, and partly in the form of ions, will be somewhere between c_1 and 1. Let y equal the fraction undissociated, and therefore $(1-y)$ the fraction dissociated. The molecular colour of the solution is then obviously given by the equation:

$$C = c_1 y + (1 - y) \quad (1).$$

Further, if K_a is the dissociation constant of the indicator acid, we have by Ostwald's law:

$$K_a y = (1 - y) \times \text{conc. H}^+ \quad (2).$$

Eliminating y from (1) and (2), we have:

$$\text{conc. H}^+ = K_a \frac{C - 1}{c_1 - C} \quad (3).$$

Hence, if we know K_a and c_1 , the relation between the molecular colour C of a solution and the concentration of hydrogen ions it contains is completely determined. K_a and c_1 can be determined by measuring the colour of solutions containing varying quantities of hydrochloric acid.

When $y=1/2$, that is, when the indicator acid is 50 per cent. dissociated, the molecular colour:

$$C = \frac{c_1 + 1}{2},$$

that is, is just midway between the two extreme colours.

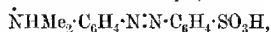
Further, equation (2) becomes:

$$K_a = \text{conc. H}^+.$$

In a solution, therefore, the colour of which is just midway between the two extreme colours, the concentration of the hydrogen ion is equal to the dissociation constant of the indicator acid. Ostwald (loc. cit.) has determined in this way the dissociation constant of a large number of indicators. He measured the concentration of the hydrogen ions by means of a hydrogen electrode. The method has the advantage when the two extreme colours of an indicator differ widely, but since only one solution can be conveniently examined,

the results are probably not very accurate, although of the right order of magnitude.

Now there is another point with regard to methyl-orange and allied indicators which has not been taken into account in the above considerations. All these compounds contain a substituted amino group, and are therefore amphoteric electrolytes. Hence in an acid solution the basic ion, for example,



may be present, as well as the undissociated molecules. To this basic ion we must assign a molecular colour, say c_2 , and its presence to any considerable extent would greatly affect conclusions drawn from colour measurements. Lundén has, in fact, criticised Veley's results adversely from this point of view, but, as will be shown later, the basic dissociation constant K_b of methyl-orange is so small that no appreciable quantity of the $\dot{\text{N}}\text{HMe}_2\text{R}$ ion is formed even in $N/20$ -hydrochloric acid. On the other hand, that of methyl-red (which differs from methyl-orange in having an ortho-carboxyl instead of a para-sulphonic group) is larger, and in consequence we find that the basic properties of this indicator have a considerable influence on the colour in solutions which are greater than $N/5000$ with respect to hydrogen ions.

If we consider solutions which contain only the basic ion and the undissociated acid, and if the fraction of the former present is y' , and therefore that of the latter is $(1-y')$, then as before:

$$C = c_2y' + c_1(1-y') \quad \dots \quad (1a).$$

Also, Ostwald's law gives:

$$K_b(1-y') = y' \times \text{conc. OH}'.$$

Since

$$\frac{\text{conc. OH}'}{\text{conc. H}'} = \frac{K_w}{K_a},$$

(K_w = dissociation constant of water), the last equation becomes:

$$\frac{K_w}{K_b}y' = (1-y') \times \text{conc. H}' \quad \dots \quad (2a).$$

These two equations are precisely similar in form to equations (1) and (2), and it is evident that we cannot decide at once, without further evidence, whether the "dissociation constant," found colorimetrically, of an amphoteric indicator is really K_a or $\frac{K_w}{K_b}$.

This is especially true when the dissociation constant is found by Salm's method. When the whole course of the colour curve is examined, it is generally possible to see at a glance whether the change of colour must be attributed to the presence of three coloured molecules (basic ion, undissociated molecule, acid ion) in the solution.

tion, or only two (compare the curves for methyl-red and methyl-orange).

EXPERIMENTAL.

To test these equations, and to determine the values of K_a and the depth of colour of methyl-orange solutions of known strength in presence of hydrochloric acid ranging from $N/20$ to $1/100,000$ has been investigated. The apparatus employed was the Donnan tintometer, used as described, for example, by Sidgwick and Tizard (Trans., 1908, **93**, 188). The standard used for comparison was a faintly acid solution of methyl-orange. It was, of course, unnecessary to know its exact strength, as it was compared before any series of measurements against a neutral solution of methyl-orange of known strength. The colours were all referred to this dilution as unit. Veley (*loc. cit.*) found it impossible to measure the depth of colour of a strongly acid (red) solution of methyl-orange by comparing it to the same standard that he used in his colour measurements with weakly acidic (orange) solutions. I found comparatively little difficulty in doing so; the difference may be partly due to the fact that whilst Veley used daylight as his illuminant, I used the yellow light from a 50 c.p. electric lamp (carbon filament).

All the solutions used were made up carefully by weight with conductivity water. They were filtered to remove dust as far as possible, and kept in steamed-out Jena-glass flasks.

It was found impossible to prepare a clear solution of methyl-orange with a concentration greater than $N/1000$. In fact, solutions of this strength were slightly turbid, but immediately cleared on dilution. The effect of dilution is to cause a slight decrease in molecular colour, as the following measurements show.

Ten c.c. of a neutral solution, $N/2000$, were taken and diluted in the tintometer tube.

| | N for methyl- orange. | Height of balancing column. |
|---------------------------------------|----------------------------|--------------------------------|
| 10 c.c. $N/2000$ solution | 2000 | 4.0 |
| " " " + 10 c.c. H_2O | 4000 | 4.3 |
| " " " + 20 c.c. H_2O | 8000 | 4.0 |
| " " " + 60 c.c. H_2O | 20,000 | 4.0 |
| " " " + a few drops $N/10$ -alkali | 20,000 | 4.0 |

This decrease in colour may be due to increasing dissociation; the presence of even a small quantity of undissociated salt may have a considerable effect on the colour. In the experiments with hydrochloric acid, the methyl-orange was used at a dilution of $\approx 20,000$, high enough to avoid complications of this kind. The standard colour measurement is important. Methyl-orange is a sodium salt; if its corresponding acid were very weak, the salt would be

considerably hydrolysed at high dilutions. This means that the solution would contain undissociated acid, which is of a much deeper colour than its ions. Addition of alkali would, in this case, diminish the colour by destroying hydrolysis. As a matter of fact, no such effect is observed, and this is strong evidence that the acid of methyl-orange cannot be very weak; on the contrary, it must be considerably stronger than acetic acid. We should therefore expect its basic dissociation constant, K_b , to be correspondingly small. These conclusions are confirmed by the colour measurements with hydrochloric acid. The latter measurements were carried out in the following way. Ten to 50 c.c. of an $N/10,000$ solution of methyl-orange were placed in the tintometer tube, a suitable quantity of a standard solution of hydrochloric acid added, and then water added up to twice the original volume of methyl-orange. The concentration of the latter was then $N/20,000$. That of the hydrochloric acid varied from $N/20$ to $N/100,000$; or, if we denote the ratio (mols. HCl) \div (mols. methyl-orange) by " a ," " a " varied from $20,000 \div 100,000 = 0.2$ to $20,000 \div 20 = 1000$.

If the height of the balancing column is h' , and the height required to balance the same amount of methyl-orange in neutral solution is h , then the molecular colour of the acid solution is given by:

$$C = \frac{h'}{h},$$

that of the neutral solution being taken as unity.

Three series of measurements were taken on different days, and with entirely fresh solutions. The temperature was 25° . The greatest deviation in the molecular colour found for any particular strength of solution was 5 per cent., the usual error being 2-3 per cent. It was found impossible to reduce the error consistently beyond this point.

The curve for methyl-orange is drawn by plotting molecular colour against concentration of hydrogen ions, the latter being expressed in inverse powers of 10. There is very little change in colour between H^+ concentrations of 10^{-7} (neutral solution) and 10^{-5} ; after this point the rise in colour is rapid—the middle part of the curve being practically a straight line—until a maximum is reached somewhere about the point conc. $\text{H}^+ = 10^{-2}$, the colour then rising about 5 per cent. in more concentrated solutions. It is obvious from the curve that these changes can be explained if we assume the presence of two coloured substances in the solution. These must evidently be the anion and the undissociated acid, and equations (1) and (2), or (3) may therefore be applied.

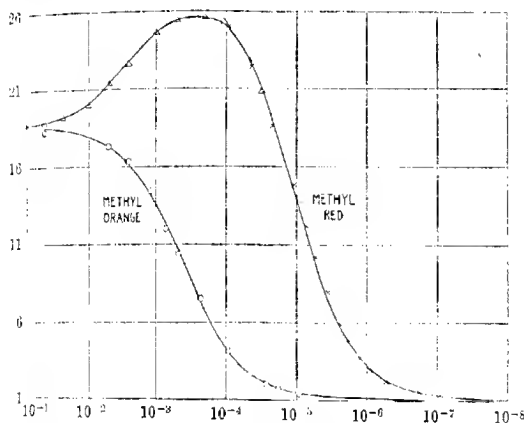
The concentration of hydrogen ions in the solutions examined is

however, by no means the same as that of the hydrochloric acid added, as Veley assumed, since the undissociated indicator acid in the solution is formed by a combination of part of the anion of the salt with hydrogen ions derived from the added hydrochloric acid. In other words, the concentration of hydrogen ion in the solution is not a/V , where V is the dilution of methyl-orange, but

$$\frac{a-y}{V},$$

y being the fraction present in the form of undissociated indicator acid.

This correction is of considerable importance, especially at the



extreme dilutions with which Veley worked, and the fact that he did not take it into account may possibly explain some of his anomalous conclusions.

Equation (2) may therefore be written in the form:

$$K_a V y = (1-y)(a-y),$$

where $V = 20,000$.

From the results, the mean values for K_a and c_1 are found to be:

$$K_a = 4.25 \times 10^{-4} \text{ (at } 25^\circ\text{)},$$

$$c_1 = 18.8.$$

The agreement between calculated and observed values is shown in the following table:

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| $\alpha = \frac{\text{mols. HCl}}{\text{mols. indicator}}$ | Conc. $\text{H}^+ = \frac{\alpha - y}{20,000}$ | y | Colour (calc.) | Colour (obs.) |
|--|--|-------|----------------|---------------|
| 0.0 | 10^{-7} * | 0.09 | (1.00) | (1.00) |
| 0.2 | $10^{-5.948}$ | 0.021 | 1.37 | 1.38 |
| 0.4 | $10^{-4.745}$ | 0.041 | 1.73 | 1.68 |
| 0.6 | $10^{-4.598}$ | 0.060 | 2.07 | 2.04 |
| 0.8 | $10^{-4.443}$ | 0.078 | 2.39 | 2.39 |
| 1.0 | $10^{-4.344}$ | 0.096 | 2.71 | 2.65 |
| 2.0 | $10^{-4.040}$ | 0.177 | 4.15 | 4.18 |
| 5.0 | $10^{-3.554}$ | 0.353 | 7.28 | 7.98 |
| 10.0 | $10^{-3.324}$ | 0.527 | 10.4 | 10.7 |
| 15.0 | $10^{-3.144}$ | 0.63 | 12.2 | 12.6 |
| 25.0 | $10^{-2.916}$ | 0.74 | 14.2 | 14.4 |
| 50.0 | $10^{-2.609}$ | 0.85 | 16.1 | 16.3 |
| 100.0 | $10^{-2.305}$ | 0.92 | 17.4 | 17.3 |
| 1000.0 | $10^{-1.200}$ | 0.99 | 18.6 | 18.3 |

* Neutral point.

Salm found $K_a = 4.6 \times 10^{-4}$ as a mean of several values ranging from 4.0 to 5.5.

The greatest deviation between the observed molecular colours and those calculated by means of the above equations is 3 per cent. It appears therefore that there is no appreciable quantity of the positive ion NMc_2R formed even when the concentration of the hydrogen ion is as high as $N/20$, for it is unlikely that the colour of this ion is the same as that of the undissociated molecule. In the parallel case of methyl-red, it is distinctly lower, as will be shown later. If we assume that not more than 1 per cent. of the methyl-orange is present in the form of the basic ion when the concentration of the hydrogen ion in the solution is 10^{-2} , we can deduce an upper limit for the basic dissociation constant from equation (2a), which gives:

$$\frac{K_a}{K_b} \times 0.01 = 0.99 \times 10^{-3},$$

or $K_b = K_a = 10^{-14}$ (at 25°).

K_b is therefore probably $< 10^{-14}$.

When α is greater than 1, the increase in colour is approximately proportional to the increase in the amount of hydrochloric acid in the solution. Thus, with each successive 0.2 molecule, the increase in colour (calculated) is 0.37, 0.36, 0.34, 0.32, 0.32. This agrees with the observations of Veley, who found that by plotting increase in colour against concentration of acid added, a straight line was obtained. The relation is, however, evidently only approximately true.

At the theoretical neutral point the concentration of hydrogen ions is 10^{-7} . Since methyl-orange does not appreciably tighten in colour below a concentration of $\text{H}^+ = 10^{-5}$, it must be considered a bad indicator for accurate volumetric analysis, apart from the fact that, since the change of colour takes place only gradually, it is

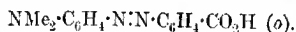
difficult to get a sharp end-point. On the other hand, the closeness of the results obtained with those required by the simple theory expressed by equations (1) and (2) shows that methyl-orange is a very good indicator to use for the quantitative colorimetric estimation of the concentration of hydrogen ions between 10^{-3} and 10^{-5} , that is, between $N/1000$ and $N/100,000$.

Substituting the values found for K_a and c_1 in (3), we get for the relation between concentration of hydrogen ions and molecular colour of methyl-orange the expression:

$$\text{conc. H}^+ = 4.25 \times 10^{-4} \frac{C-1}{18.8-C}$$

Methyl-red.

In order to throw further light on the colour changes of indicators which are amphoteric electrolytes, a series of similar colour measurements were made with methyl-red, an indicator discovered by Rupp and Loose (*Ber.*, 1908, **41**, 3905). Its constitution is expressed by the formula:



The method of preparation given by these authors is not satisfactory, only small yields being obtainable. The following method is recommended by Mr. T. F. Winmill, who kindly supplied me with the indicator in the first place.

Five grams of anthranilic acid are dissolved in 150 c.c. of water and 15 c.c. of concentrated hydrochloric acid. To this, 2.5 grams of solid sodium nitrite are added, and the solution kept for half an hour. It is then poured into a solution of 4.65 grams of dimethylaniline in a mixture of 5 c.c. of concentrated hydrochloric acid and 50 c.c. of water. Fifty grams of sodium acetate are added. On warming to 40° , the red product quickly separates, but the reaction does not appear to be complete for about three hours. The substance is then collected, and can be crystallised from glacial acetic acid. The yield is almost quantitative.

Methyl-red is very insoluble in water; its saturated solution at the ordinary temperature is only about $N/100,000$. Since it contains a carboxyl instead of a sulphonic group, we should expect it to be a weaker acid than methyl-orange, and a correspondingly stronger base. In accordance with this, methyl-red is easily soluble both in acids and in alkalis. Its alkali salts are surprisingly soluble; the potassium salt can only be obtained by evaporating an alcoholic solution to dryness, since it is soluble to a considerable extent in ether, and deliquescent in air. Since the sodium salt of helianthin (methyl-orange) is somewhat insoluble in water, the difference in behaviour is striking.

The pure potassium salt appears to dissolve completely in a very small quantity of water, forming a very deep red solution; on diluting further, the acid separates out. The hydrolysis appears to be excessive if we accept the value for the dissociation constant of the acid (10^{-5}), found from the colour measurements, but since the solubility of the acid is so small, the appearance may be deceptive. It would probably be interesting to investigate further the behaviour of the alkaline salts of this indicator, but this does not come within the scope of the present paper.

Since a clear neutral solution of the salt could not be obtained, the saturated solution of the acid was used in the colour measurements. Its strength was found approximately in the following way. A known quantity of the potassium salt was dissolved in a slight excess of alkali, so as to make an $N/1000$ -solution; 10 c.c. of this were then diluted to 1 litre. This $N/100,000$ -solution contained, of course, a slight, but only a slight, excess of alkali. Ten c.c. were placed in the tintometer tube, the same volume of $N/1000$ -hydrochloric acid added, and the colour was measured. Ten c.c. of the saturated solution of the acid + 10 c.c. of $N/1000$ -hydrochloric acid were then measured in the same way. It makes no difference if the concentration of hydrogen ions in this solution was slightly greater than that in the salt solution, for, as will be shown later, the molecular colour is at a maximum at this point, and does not change appreciably between H^+ concentrations of $N/5000$ and $N/2000$ (see the curve for methyl-red).

Since the depth of colour of the two solutions was approximately the same, the strength of the acid solution was taken to be roughly the same as that of the salt solution, namely, $N/100,000$. The saturated solution was usually diluted in the tube up to about four times its original volume.

It has already been pointed out in discussing the results with methyl-orange, that the concentration of the hydrogen ions in a very dilute solution of hydrochloric acid containing an indicator, is not the same as that of the hydrochloric acid itself, but is less or greater, as the case may be. In order to allow properly for this we must, of course, know exactly the quantity of indicator present. The uncertainty of the actual dilution of the methyl-red used makes, therefore, experiments with hydrochloric acid untrustworthy when the concentration of the latter falls below a certain amount. For this reason, the most dilute solution of hydrochloric acid used in this and more concentrated solutions was taken to be the same as that of the hydrochloric acid present. The remainder of the curve was determined by measuring the colour in solutions of

sodium acetate containing varying amounts of acetic acid. The concentration of the sodium acetate was $N/500$; that of the hydrogen ions, when a certain amount of acetic acid, equal to n times that of the sodium acetate, is added, may then be easily calculated by means of Ostwald's law, the dissociation constant of acetic acid at 18° (the temperature of measurement) being taken as 1.8×10^{-5} . Hence:

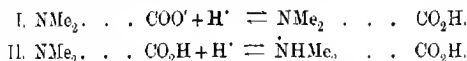
$$1.8 \times 10^{-5} \times \text{conc. HA} = \text{conc. A}' \times \text{conc. H}'.$$

Since we may assume the sodium acetate to be completely dissociated, the equation becomes:

$$\begin{aligned} \text{conc. H}' &= 1.8 \times 10^{-5} \times \frac{\text{HA}}{\text{NaA}}, \\ &= n \times 1.8 \times 10^{-5}. \end{aligned}$$

Since the amounts of acetic acid and sodium acetate in the solution are always large compared to that of the indicator, the correction that must be made when strong acids, such as hydrochloric acid, are used is unnecessary.

The colour curve obtained in this way is shown on p. 2483. The lower part of the curve is similar to that of methyl-orange, but the colour falls again when the concentration of hydrogen ions is greater than $N/2000$ or thereabouts. We must therefore assume that two changes take place:



The colours of the acid ion, undissociated molecule, and basic ion are taken, as before, as 1, c_1 , and c_2 respectively. Since the minimum is very flat, the first change must be nearly complete before the second begins. Disregarding the latter for the present, then, we may apply the equations:

$$\begin{aligned} C' &= c_2 y + (1 - y), \\ K'_a y &= (1 - y) \times \text{conc. H}', \end{aligned}$$

to the lower part of the curve, the concentration of hydrogen ions being calculated in the ways already indicated. For the mean values of K'_a and c_1 , we find:

$$\begin{aligned} K'_a &= 1.05 \times 10^{-5}, \\ c_1 &= 27.6. \end{aligned}$$

The temperature was in this case 18° .

The following table contains the results so obtained:

*Molecular Colour of Methyl-red.*1.—*Experiments with Mixtures of Sodium Acetate and Acetic Acid.*

| $\frac{\text{HA}}{\text{NaA}}$ | Conc. H ⁺ | Colour (obs.). | Colour (calc.). |
|--------------------------------|----------------------|----------------|-----------------|
| 0.0 | $10^{-8.272}$ | 1.10 | 1.02 |
| 0.005 | $10^{-7.946}$ | 1.26 | 1.22 |
| 0.01 | $10^{-7.745}$ | 1.46 | 1.46 |
| 0.03 | $10^{-7.268}$ | 2.24 | 2.30 |
| 0.05 | $10^{-6.936}$ | 3.00 | 3.10 |
| 0.07 | $10^{-5.960}$ | 3.68 | 3.81 |
| 0.1 | $10^{-5.745}$ | 4.86 | 4.88 |
| 0.13 | $10^{-5.624}$ | 5.86 | 5.84 |
| 0.2 | $10^{-5.444}$ | 7.84 | 7.78 |
| 0.3 | $10^{-5.268}$ | 10.2 | 10.2 |
| 0.4 | $10^{-5.143}$ | 12.2 | 11.8 |
| 0.6 | $10^{-4.967}$ | 14.8 | 14.5 |
| 1.2 | $10^{-4.696}$ | 18.6 | 18.9 |
| 2.4 | $10^{-4.361}$ | 22.0 | 22.4 |
| 5.0 | $10^{-4.046}$ | 25.2 | 24.8 |

2.—*Experiments with Hydrochloric Acid up to N/2000.*

| V_{HCl} | Conc. H ⁺ | Colour (obs.). | Colour (calc.). |
|------------------|----------------------|----------------|-----------------|
| 31,000 | $10^{-4.401}$ | 19.9 | 21.0 |
| 21,000 | $10^{-4.222}$ | 22.3 | 22.8 |
| 11,000 | $10^{-4.101}$ | 24.9 | 24.8 |
| 9000 | $10^{-3.954}$ | 25.4 | 25.3 |
| 5000 | $10^{-3.899}$ | 25.6 | 26.2 |
| 2000 | $10^{-3.790}$ | 25.6 | 27.0 |

The observed and calculated values closely agree; in particular the two series of measurements agree well where they overlap. The last colour measurement (in $N/2000$ -hydrochloric acid) is considerably below the calculated value; this is due to the formation of the basic ion. In still higher concentrations of hydrogen ions, the colour sinks further, until it again becomes practically constant when conc. H⁺ is greater than $N/20$. Equations (1a) and (2a) apply to this case. If we assume that no acid dissociation takes place, we get:

$$C = y_2 c_2 + (1 - y_2) c_1$$

where y_2 is the fraction of the indicator present in the basic form, and c_2 is the molecular colour of the basic ion; c_1 has already been found to be 27.6.

Also, if K_b is the basic dissociation constant of the indicator:

$$\frac{K_b}{K_a} y_2 = (1 - y_2) \text{conc. H}^+$$

From the colour measurements, we find:

$$\frac{K_b}{K_a} = 2.0 \times 10^{-3}.$$

$$c_2 = 18.6.$$

Molecular Colour of Methyl-red in Solutions of Hydrochloric Acid greater than N/5000.

| V_{HCl} . | Conc. H^+ . | Colour (obs.). | Colour (calc.). |
|-------------|---------------|----------------|-----------------|
| 2 | $10^{-0.3}$ | 18.4 | 18.6 |
| 10 | $10^{-1.9}$ | 18.8 | 18.8 |
| 20 | $10^{-1.3}$ | 18.8 | 18.9 |
| 30 | $10^{-1.5}$ | 18.9 | 19.1 |
| 40 | $10^{-1.60}$ | 19.2 | 19.2 |
| 100 | $10^{-2.90}$ | 19.9 | 20.0 |
| 210 | $10^{-2.622}$ | 21.6 | 21.4 |
| 410 | $10^{-2.642}$ | 23.0 | 22.6 |
| 1000 | $10^{-3.140}$ | 24.8 | 24.6 |
| 2000 | $10^{-3.391}$ | 25.6 | 25.8] |
| 5000 | $10^{-3.699}$ | 25.6 | 26.7] |

The dilutions $V_{HCl} = 2000$ and 5000 require further consideration; it is evident that the molecular colours at and between these dilutions cannot strictly be calculated on either of the assumptions: (1) that no basic ion is present, (2) that no acid ion is present. Both these ions as well as the undissociated molecule must be present to an appreciable extent. By using the dissociation constants given above, we can calculate the amount of these ions present, and thus arrive at the following results:

| V_{HCl} . | Acid ion. ($1 - y_1 - y_2$) | Undiss. mol. y_1 | Basic ion. y_2 | Col. (calc.). | Col. (obs.). |
|-------------|----------------------------------|-----------------------|---------------------|---------------|--------------|
| 2000 | 0.015 | 0.788 | 0.197 | 25.4 | 25.6 |
| 5000 | 0.045 | 0.868 | 0.087 | 25.6 | 25.6 |

Hence the whole course of the colour curve is satisfactorily accounted for.

Since $K_{10} = 0.6 \times 10^{-14}$ at 18° ,

$$\text{we have } K_b = \frac{0.6 \times 10^{-14}}{2 \times 10^{-3}} = 3 \times 10^{-12}.$$

It must not, of course, be assumed that the colours of methyl-orange and methyl-red are the same in equivalent alkaline solution, because the molecular colours of both the acid ions have been taken as unity. As a matter of interest, however, it may be mentioned that, as far as could be judged, the difference between the two depths of colour of the two acid ions is but small.

As an indicator methyl-red is greatly superior to methyl-orange, as the colour curves show. The visible change, red to yellow, takes place between $10^{-5.7}$ and 10^{-7} , that is, between H^+ concentrations of $N/200,000$ and $N/10,000,000$. Not only therefore is the end-point very much sharper than when methyl-orange is used, but the neutral point so found is very much nearer the theoretical neutral point. Methyl-red is, in fact, an extremely sensitive indicator, and should come into extended use; it is especially valuable for the

exact titration of moderately weak bases (such as ammonia) by strong acids.

As a means for measuring colorimetrically the concentration of hydrogen ions in a solution, methyl-red would probably be found valuable when such concentration lies between 10^{-5} and 10^{-4} . Methyl-orange cannot be used when conc. H^+ is greater than 10^{-3} . If methyl-red is used for this purpose, it would be advisable to refer all molecular colours to the maximum colour found when conc. H^+ lies between $N/2000$ and $N/5000$; this maximum colour can be measured very accurately, whilst the extreme yellow colour of the ion is somewhat difficult to measure. Taking the maximum colour as 25.6, the theoretical colour of the undissociated molecule is 27.6, and the relation between concentration of hydrogen ions (between $10^{-4.5}$ and $10^{-6.5}$, say) and the molecular colour of the solution can be expressed by the equation:

$$\text{conc. } H^+ = \frac{1.05 \times 10^{-5}(C-1)}{27.6-C}.$$

Summary.

The depths of colour of methyl-orange and methyl-red in solutions of varying concentrations of hydrogen ions have been measured.

From the results, the following constants have been deduced:

| | K_a | K_b |
|---|-----------------------|---------------------|
| Methyl-orange (at 25°): $NMe_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot SO_3H$ | 4.25×10^{-4} | $< 10^{-14}$ |
| Methyl-red (at 18°): $NMe_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot CO_2H$ (o) | 1.05×10^{-3} | 3×10^{-13} |

The value of methyl-red as an indicator is discussed.

Expressions are given connecting the depths of colour of methyl-orange and methyl-red solutions with the concentrations of hydrogen ion in the solutions.

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CCXVI.—The Hydrolysis of Aniline Salts Measured Colorimetrically.

By HENRY THOMAS TIZARD.

In the preceding paper it was shown that the concentration of hydrogen ions in a solution of methyl-orange, the molecular colour of which is C , is given by the equations:

$$\begin{aligned} C &= 18.8y + (1-y) \dots \dots \dots (1) \\ 4.25 \times 10^{-4}y &= (1-y) \times \text{conc. } H^+ \dots \dots \dots (2) \end{aligned}$$

where y denotes the fraction of methyl-orange present in the form of undissociated indicator acid.

These equations have now been used to determine colorimetrically the degree of hydrolysis of aniline salts.

Aniline Hydrochloride.

Aniline hydrochloride was prepared by mixing equivalent quantities of pure concentrated hydrochloric acid and aniline, which was purified in the way recommended by Hantzsch and Freese (*Ber.*, 1894, 27, 2966). The salt was recrystallised from water slightly acidified with hydrochloric acid. The colour measurements were made in exactly the same way as that described in the preceding paper. The temperature of observation was 25°. One of the chief objections to the measurement of hydrolysis by colorimetric observations seems to be the difficulty of keeping the temperature constant. It was found best to keep the solutions until just before use in a thermostat at the required temperature, and then to transfer the requisite amount quickly to the tintometer tube. Since with a certain amount of practice accurate colour measurements can be made very rapidly, the temperature alters only slightly during the actual experiment. In the experiments communicated in this paper, it certainly did not vary sufficiently to affect the colour outside the unavoidable error of observation.

The dilutions examined ranged from 1/20- to 1/1200-normal.

In a pure aqueous solution of a salt of a weak base, the concentration of the hydrolysed base is, of course, equal to that of the free hydrogen ions in the solution. When, however, an indicator, such as methyl-orange, is also present in the solution, it partly combines with the hydrogen ions, and the concentration of the latter will therefore be less than that of the hydrolysed base. Thus, if x is the fraction of salt hydrolysed, V_1 the dilution of the salt, V_2 that of the indicator, and y (as before) the fraction of the latter present in the form of undissociated acid:

$$\frac{x}{V_1} = \text{conc. aniline} \\ - \text{conc. H}^+ + \frac{y}{V_2}.$$

This correction is of considerable importance when hydrolysis is large and the dilution of the indicator not too great. Thus, to take an example from the following table, when $V_1=200$ and $V_2=20,000$, the molecular colour is found to be 8.63. From equations (1) and (2) we get:

$$y=0.429, \text{ conc. H}^+=3.19 \times 10^{-4};$$

hence

$$\begin{aligned}\text{conc. aniline} &= 3.19 \times 10^{-4} + \frac{0.429}{20,000} \\ &= 3.40 \times 10^{-4}.\end{aligned}$$

The difference between the two concentrations is thus 7 per cent. It was not taken into account by Veley in researches of a similar nature, and this, together with the reasons already put forward in the previous paper, may explain the frequent difference between his results and those arrived at by other methods.

The hydrolysis constant is given by the equations:

$$\frac{K_{10}}{K_b} = \frac{\text{conc. } C_6H_5 \cdot NH_2 \times \text{conc. } H^+}{\text{conc. } C_6H_5 \cdot NH_3} = \frac{x}{1-x} \times \text{conc. } H^+.$$

The following table contains the results obtained:

| V_1 | V_2 | Colour (C). | $y = \frac{C \cdot 1}{17.8 \cdot \text{conc. } H^+ \times 10^4 \cdot 100x}$ | $\frac{K_{10}}{K_b} \times 10^4$ | | |
|-------|--------|-------------|---|----------------------------------|------|---------|
| 20 | 20,000 | 12.6 | 0.652 | 7.94 | 1.65 | (0.133) |
| 30 | 30,000 | 11.9 | 0.612 | 6.71 | 2.07 | (0.142) |
| 40 | 40,000 | 11.4 | 0.584 | 5.97 | 2.51 | (0.154) |
| 60 | 30,000 | 10.7 | 0.545 | 5.09 | 3.16 | (0.176) |
| 80 | 20,000 | 10.4 | 0.523 | 4.76 | 4.12 | (0.204) |
| 100 | 30,000 | 9.86 | 0.498 | 4.21 | 4.38 | (0.183) |
| 200 | 20,000 | 8.63 | 0.420 | 3.19 | 6.80 | 0.210 |
| 300 | 15,000 | 7.84 | 0.384 | 2.65 | 8.73 | 0.253 |
| 400 | 20,000 | 6.97 | 0.335 | 2.14 | 9.24 | 0.218 |
| 500 | 20,000 | 6.63 | 0.316 | 1.96 | 10.6 | 0.232 |
| 600 | 15,000 | 6.25 | 0.295 | 1.78 | 11.9 | 0.210 |
| 800 | 13,333 | 5.86 | 0.273 | 1.59 | 14.3 | 0.263 |
| 1000 | 20,000 | 5.48 | 0.252 | 1.43 | 15.6 | 0.264 |
| 1200 | 20,000 | 4.92 | 0.220 | 1.20 | 15.7 | 0.223 |

A 2 per cent. error in colour measurement corresponds on an average with an error in the hydrolysis constant of 10 per cent., so that the fluctuations of the constant from the mean value for the last eight dilutions are within the error of observations, and, moreover, are not materially greater than those found when other methods of measurement are employed. The actual mean value of the constant for these eight dilutions is:

$$\frac{K_{10}}{K_b} = 0.242 \times 10^{-4},$$

whereas Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 239) found by conductivity measurements:

$$\frac{K_{10}}{K_b} = 0.24 \times 10^{-4}.$$

The two values are thus practically identical.

At higher concentrations, however, the constant is very much smaller, and appears to increase quite regularly with the dilution. This difference is too great to be accounted for by the incomplete

dissociation of the aniline hydrochloride, and as the behaviour has not been observed when other methods are used, it is presumably due to the formation of a compound with methyl-orange, which affects the colour to a small extent. With aniline acetate, however, no such phenomenon was observed; the colour in a $N/20$ -solution of this salt is perfectly normal. The so-called neutral salt action discussed by Szyszkowski (*Zeitsch. physikal. Chem.*, 1910, **73**, 269) is apparently unconnected with the above phenomenon, for methyl-orange appears to indicate a higher concentration of hydrogen ion in presence of sodium chloride than the solution contains, whereas the reverse is true with aniline hydrochloride.

On the whole, it is perhaps inadvisable to use concentrated solutions of salts in colour measurements of this kind.

Aniline Acetate.

This salt has apparently not been prepared in the solid state. A mixture of equivalent weights of pure aniline and acetic acid will not solidify when cooled to -20° , but as the liquid is extremely viscous at this temperature, it is probably supercooled. If the equivalent mixture is kept for some time, acetanilide is formed. The solution used in these experiments was therefore made by mixing equivalent quantities of $N/5$ -aniline and $N/5$ -acetic acid, both of which were made up accurately by weight from the pure substances.

In a solution of a salt of a weak acid and a weak base, the dissociation constants of which are K_a and K_b respectively, let γ be the degree of dissociation of the salt, and x the fraction hydrolysed; then Ostwald's law gives the two equations:

$$\begin{aligned} K_a x &= (1-x) \times \text{conc. H}^+ \\ K_b x &= (1-x) \times \text{conc. OH}^-; \end{aligned}$$

hence:

$$\frac{K_a K_b x^2}{\gamma^2 (1-x)^2} = K_w,$$

or:

$$\frac{x}{\gamma(1-x)} = \sqrt{\frac{K_w}{K_a K_b}}.$$

This is the well-known equation for the hydrolysis of such a salt; it signifies that when the salt is completely dissociated ($\gamma=1$), the degree of hydrolysis is independent of the dilution. It has not, however, yet been pointed out, so far as I know, that the concentration of the hydrogen (and hydroxyl) ions in a solution of a weak salt must always be constant, whatever be the dilution, and

whether the salt is completely dissociated or not. This follows at once from the above equations, for

$$\text{conc. H}^+ = \frac{K_a x}{\gamma(1-x)} = \sqrt{\frac{K_w K_a}{K_b}} = \text{constant.}$$

A striking proof of this can be obtained colorimetrically. The addition of a few drops of the aniline acetate solution to a neutral solution of methyl-orange causes the same rise in colour as the addition of a large quantity. The results of actual experiments are shown below:

| Aniline acetate. | Colour. | Mean. | conc. H ⁺ . | x (For complete dissociation.) |
|------------------|---------|-------|------------------------|----------------------------------|
| 20 | 1.92 | — | — | — |
| 40 | 1.92 | — | — | — |
| 50 | 1.90 | — | — | — |
| 80 | 1.90 | 1.91 | 0.229×10^{-4} | 0.569 |
| 100 | 1.90 | — | — | — |
| 200 | 1.91 | — | — | — |
| 500 | 1.90 | — | — | — |

The molecular colour is constant within the errors of observation when the concentration of aniline acetate varies from $N/20$ to $N/500$. From the colour, the concentration of the hydrogen ion is obtained as before, and then the degree of hydrolysis is calculated from the equation:

$$\frac{x}{1-x} = \frac{\text{conc. H}^+}{K_a},$$

K_a being 1.8×10^{-5} .

In this way we find $x=56.0$ per cent. Arrhenius and Walker (*Zeitsch. physikal. Chem.*, 1889, 5, 18) found that for the same salt the percentage hydrolysed was 55.5, as a mean of the values, for six different dilutions ranging from $V=12.5$ to $V=400$.

The two methods therefore give practically identical results.

From the hydrolysis of the chloride, we can calculate:

$$K_b = \frac{K_w}{0.24 \times 10^{-4}} = \frac{1.1}{0.24} \times 10^{-10} \quad (K_w = 1.1 \times 10^{-14} \text{ at } 25^\circ)$$

$$= 4.6 \times 10^{-10}$$

from that of the acetate:

$$K_b = \frac{K_w K_a}{(\text{conc. H}^+)^2} = \frac{1.1 \times 10^{-14} \times 1.8 \times 10^{-5}}{0.0522 \times 10^{-8}} = 3.8 \times 10^{-10}.$$

This difference is within the error of hydrolysis measurement by any method. The colorimetric method used in the investigation seems to give too low values for the hydrolysis constant of the hydrochloride, so that K_b calculated from the hydrolysis of the acetate is probably more accurate. In any case the mean value:

$$K_b = 1.2 \times 10^{-10} \text{ at } 25^\circ$$

cannot be far from the truth. The number accepted by Lundén (4.6×10^{-10}) appears therefore too high.

In conclusion, the results communicated in the present paper show that, with proper precautions, hydrolysis can be measured colorimetrically by means of methyl-orange, with an accuracy that compares favourably with that attained by other methods. The base should, however, have a dissociation constant less than 10^{-7} . For bases stronger than this, but weaker than ammonia, methyl-red will probably be found suitable. Since the apparatus and the method of working are extremely simple, there is no reason why the colorimetric method should not come into more extended use.

Summary.

It is shown that the degree of hydrolysis of aniline salts can be accurately determined by measuring the depth of colour of methyl-orange in the solution, and then calculating the concentration of hydrogen ions by means of the equations deduced in the preceding paper.

It is also pointed out that the concentration of hydrogen ions in a solution of a salt of a weak acid and a weak base is always the same, whatever the dilution and degree of dissociation of the salt.

The researches communicated in this and the preceding paper were carried out in the Davy-Faraday Laboratory of the Royal Institution. I should like to express here my thanks to the managers of the laboratory for the facilities they have placed at my disposal.

DAVY-FARADAY LABORATORY,
ROYAL INSTITUTION.

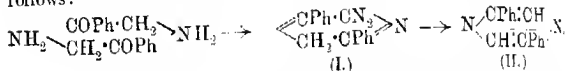
[CCLVII.—*Syntheses in the Epinephrine Series. Part II.* *The Formation and Properties of Some 2:5- and* *2:6-Substituted Pyrazines and their Conversion* *into Amino-ketones and Imino-diketones.*

By FRANK TUTIN.

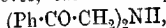
In a recent communication (Tutin, Caton, and Haun, *Trans.*, 1909, 15, 2113) it was shown that the action of ammonia on *o*-chloro-dihydroxyacetophenone did not result in the formation of *o*-amino-dihydroxyacetophenone, but yielded only resinous products. This result was considered somewhat remarkable, inasmuch as the analogous chloro-*mp*-dihydroxy-ketone readily yields the corresponding amine (D.R.-P. 155632). The behaviour of a number of

o-chloroacetophenone derivatives on heating with ammonia has therefore been investigated, with the result that it has been rendered evident that these compounds may be divided into three classes, according to the products which they yield on this treatment. Thus, *o*-chloro-*mp*-dihydroxyacetophenone, on treatment with ammonia, behaves in a normal manner, yielding the corresponding amine. Only amorphous products result from the interaction of ammonia and *o*-chloro-*p*-hydroxyacetophenone, *o*-chloro-*o*-methoxyacetophenone, or *o*-chloro-*op*-dimethoxyacetophenone. When, however, either *o*-chloroacetophenone, *o*-chloro-*p*-methoxyacetophenone, or *o*-chloro-*mp*-dimethoxyacetophenone is heated with alcoholic ammonia, the principal product of the reaction is a mixture of 2: 5- and 2: 6-substituted pyrazines, in about equal proportions.

The formation of 2: 5-diphenylpyrazine (II) from *o*-bromoacetophenone and ammonia was studied by Gabriel (*Ber.*, 1908, 41, 1127), who showed that, after replacement of the halogen, 3: 6-dihydro-2: 5-diphenylpyrazine (I) was formed, and that this then underwent spontaneous oxidation to the diphenylpyrazine, as follows:

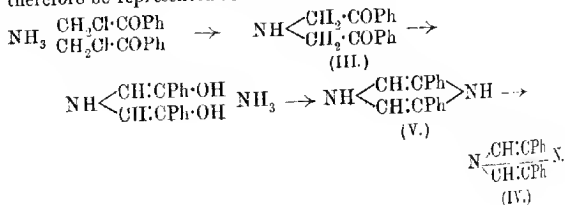


The last-mentioned author, however, overlooked the fact that 2: 6-diphenylpyrazine is also formed in this reaction, and the mode of production of this compound therefore remains to be explained. Gabriel (*loc. cit.*), however, identified diphenacylamine,

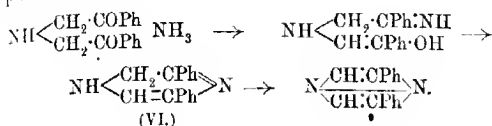


as a product of the interaction of *o*-bromoacetophenone and ammonia, and the present author has similarly obtained this base, as a minor product, from *o*-chloroacetophenone.

It is now shown that diphenacylamine (III) and its derivatives are intermediate compounds in the formation of 2: 6-substituted pyrazines, for they pass into the latter on heating with ammonia. The series of changes which results in the formation of 2: 6-diphenylpyrazine (IV) from *o*-chloroacetophenone and ammonia may therefore be represented as follows:



According to this scheme the action of ammonia on diphenacylamine first results in the production of 1: 4-dihydro-2: 6-diphenylpyrazine (V), which then passes into 2: 6-diphenylpyrazine by spontaneous oxidation. The change might, however, conceivably take place as follows:



If this be the case, the intermediate compound will be 3: 4-dihydro-2: 6-diphenylpyrazine (VI).

The change which is here shown to occur on heating compounds of the type $(\text{R} \cdot \text{CO} \cdot \text{CH}_2)_3\text{NH}$ with ammonia does not appear to have been observed before, and it therefore seems to afford a new, general method for the production of 2: 6-substituted pyrazines.

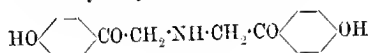
The interaction of ammonia and ω -chloro-*p*-methoxyacetophenone proceeds similarly to that of ω -chloroacetophenone and ammonia, yielding, as principal products, *pp'*-dimethoxy-2: 5-diphenylpyrazine (m. p. 223°) and *pp'*-dimethoxy-2: 6-diphenylpyrazine (m. p. 137.5°). The former of these two compounds is of particular interest, as, on fusion, it passes into the "liquid-crystalline" state, and this phase persists over an exceptionally large range of temperature, namely, 414°. *pp'*-Dimethoxy-2: 5-diphenylpyrazine therefore represents a new addition to the already considerable list of "liquid-crystalline" anisyl derivatives, but it appears to be the first compound of this class in which the anisyl group is attached to a ring. A further interesting property of *pp'*-dimethoxy-2: 5-diphenylpyrazine is that its solutions exhibit a violet-blue fluorescence, a behaviour which has not previously been observed amongst pyrazine derivatives. Furthermore, on the addition of a drop of concentrated hydrochloric or sulphuric acid to a chloroform solution of this base, a most brilliant green fluorescence is produced. *pp'*-Dimethoxy-2: 6-diphenylpyrazine behaves in marked contrast to its 2: 5-substituted isomeride, as it fluoresces but slightly, and only in neutral solution, and it does not pass into the "liquid-crystalline" state.

ω -Chloro-*mp*-dimethoxyacetophenone yielded *mm'*-*pp'*-tetramethoxy-2: 5-diphenylpyrazine (m. p. 208°) and *mm'*-*pp'*-tetramethoxy-2: 6-diphenylpyrazine (m. p. 160°) on treatment with ammonia, neither of which passes into the "liquid-crystalline" state. The former compound is, however, strongly fluorescent, but only in neutral solution.

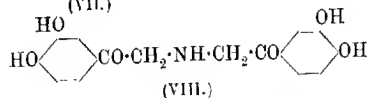
It is furthermore shown in the present communication that the series of changes which result respectively in the formation of

2:5-substituted pyrazines from ω -aminoacetophenone or its derivatives, and in the conversion of diphenacylamine or its derivatives into 2:6-substituted pyrazines, may be reversed by means of hydriodic acid. Thus, when 2:5-diphenylpyrazine is heated with hydriodic acid, reduction followed by hydrolysis occurs, resulting in the formation of two molecules of ω -aminoacetophenone-hydriodide. Similarly, 2:6-diphenylpyrazine, when analogously treated, is converted into *diphenacylamine hydriodide* and ammonium iodide. Of course, when employing the pyrazine derivatives containing methoxyl groups, the methyl group is also eliminated by the hydriodic acid. This reaction therefore has afforded a new method of preparing ω -amino-*p*-hydroxyacetophenone and ω -amino-*mp*-dihydroxyacetophenone, two bases which are of interest on account of their physiological activity. The former of these bases was previously prepared by the present author in conjunction with Messrs. Caton and Hann (*loc. cit.*) from ω -chloro-*p*-acetoxyacetophenone, whilst the latter base is of special importance on account of its near relationship to epinephrine.

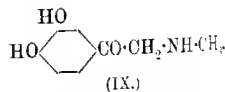
pp'-Dihydroxydiphenacylamine and *mm'*-*pp'*-tetrahydroxydiphenacylamine have been prepared by the action of hydriodic acid on the previously-mentioned methoxy-2:6-diphenylpyrazines. It will readily be seen from a comparison of the formulæ given below that *pp'*-dihydroxydiphenacylamine (VII) and, especially, *mm'*-*pp'*-tetrahydroxydiphenacylamine (VIII) are closely related to the ketone derived from epinephrine (IX), as also to the above-mentioned two ω -aminohydroxyacetophenones:



(VII.)



(VIII.)



(IX.)

It was therefore to be expected that these two diphenacylamine derivatives would be possessed of physiological activity, and their properties have accordingly been investigated in the Wellcome Physiological Research Laboratories by Dr. H. H. Dale, to whom the author is indebted for the following and the subsequently mentioned physiological experiments. It was found that each of these compounds, in the form of salts, when injected intravenously into cats, caused a rise in blood-pressure, *pp'*-dihydroxydiphenacyl-

amine (VII) having an action similar to that of the related compound, *o*-amino-*p*-hydroxyacetophenone (Tutin, Caton, and Hann, *loc. cit.*), whilst the corresponding tetrahydroxy-base (VIII) had a greater activity, more resembling that of the ketone derived from epinephrine (IX).

It has already been mentioned that *o*-chloro-*o*-methoxyacetophenone and *o*-chloro-*op*-dimethoxyacetophenone yield only amorphous products when heated with ammonia, whereas the analogous compounds containing the methoxyl groups in the *m*- and *p*-positions readily yield substituted pyrazines. It therefore appears that the presence of a methoxyl group in the *o*-position with respect to the side-chain precludes the formation of pyrazines from *o*-chloroacetophenone derivatives, although the reason for this is not apparent.

On account of the above-mentioned property of the *o*-substituted *o*-chloroacetophenone derivatives here described, it was impossible to obtain from them the corresponding *o*-aminohydroxyacetophenones in the way which has already been noted in connexion with the preparation of *o*-amino-*p*-hydroxyacetophenone from *o*-chloro-*p*-methoxyacetophenone. Recourse was therefore had to the use of potassium phthalimide, and by this means derivatives and salts of *o*-amino-*o*-hydroxyacetophenone and *o*-amino-*op*-dimethoxyacetophenone have been obtained. When examined physiologically, the *hydriodide* of the *o*-hydroxy-base was found to be practically inactive, whilst the corresponding salt of the *op*-dimethoxy-base had no greater activity than the analogous *p*-hydroxy-compound. It is therefore seen that hydroxyl groups in the *o*-position with respect to the side-chain are devoid of physiological activity in the class of compounds under consideration, a result which is in harmony with a previous observation of Dr. Dale, who

found *o*-hydroxy- β -phenylethylamine, $\begin{matrix} \text{OH} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \end{matrix}$, to be inert, whilst the analogous *p*-compound is strongly active (Barger, *Trans.*, 1909, **95**, 1123).

o-Chloro-*o*-methoxyacetophenone is formed, together with the corresponding *p*-compound, by the action of aluminium chloride on chloroacetyl chloride and anisole. The further action of aluminium chloride on *o*-chloro-*o*-methoxyacetophenone results in the formation of *o*-chloro-*o*-hydroxyacetophenone. The latter substance differs from the corresponding *p*-compound, inasmuch as it is quite insoluble in aqueous sodium carbonate, thus showing how the relative positions of the groups in the benzene nucleus affect the acidity of the hydroxyl group.

The above-mentioned substituted *o*-aminoacetophenones, containing a hydroxyl group in the *o*-position with respect to the side-chain,

differ markedly in their properties from the previously-mentioned analogous compounds which are substituted in the *m*- or *p*-position, inasmuch as they condense and oxidise, when dissolved in neutral solvents, to form 2:5-substituted pyrazines. *oo'*-Dihydroxy-2:5-diphenylpyrazine and *oo'*pp'-tetrahydroxy-2:5-diphenylpyrazine have thus been prepared.

The two *o*-substituted ω -aminoacetophenones described also show a singular behaviour when benzoylated, either by the Schotten-Baumann method or in pyridine solution, for, when thus treated, they yield benzoyl derivatives of internal anhydrides. It would appear possible that these condensation products are 1-benzoyl-indoxyl and 6-benzoyloxy-1-benzoylindoxyl respectively.

Gabriel (*loc. cit.*), from his work on ω -aminoacetophenone, concluded that α -amino-ketones of this type were incapable of existence in the free state, but always underwent condensation when liberated from their salts. It is evident, however, from the results given in the present paper that this is not invariably the case. Thus, ω -aminoacetophenone, ω -amino-*p*-methoxyacetophenone, ω -amino-*mp*-dimethoxyacetophenone, and ω -amino-*o*-hydroxyacetophenone condense spontaneously, yielding pyrazine derivatives in the manner shown by Gabriel. ω -Amino-*p*-hydroxyacetophenone and ω -amino-*mp*-dihydroxyacetophenone, on the other hand, cannot be caused to condense; whilst ω -amino-*op*-dihydroxyacetophenone possesses properties between those of these two groups, for it can be obtained in the free state, although it condenses somewhat readily.

EXPERIMENTAL.

Interaction of ω -Chloroacetophenone and Ammonia.

Chloroacetyl chloride was dissolved in an excess of benzene, and one molecular proportion of aluminium chloride added. A violent reaction ensued, and, when this had subsided, ice and hydrochloric acid were added. The aqueous layer was then separated, and, after washing the benzene solution with water, the greater part of the solvent was removed from it. On adding light petroleum to the concentrated liquid thus obtained, ω -chloroacetophenone separated in glistening plates, melting at 59°. The yield was nearly quantitative.

Fifteen grams of ω -chloroacetophenone were heated for one and a half hours at 100° in sealed tubes with an excess of alcoholic ammonia. After allowing the contents of the tubes to cool, the solid which had separated was collected, washed with alcohol, and then extracted repeatedly with boiling xylene. The material undissolved by this treatment consisted entirely of ammonium chloride, but on concentrating the xylene extracts, a compound

separated in plates, melting at 194° . As thus obtained, this substance possessed a dark bluish-green colour, and was only obtained colourless after being treated, in acetic acid solution, with a small amount of potassium permanganate dissolved in the same solvent. When crystallised from xylene after this treatment, it formed large, colourless plates, melting at 194° , and was identified as 2: 5-diphenylpyrazine (Found, $C=79.5$; $H=5.1$. Calc., $C=79.3$; $H=5.0$ per cent.)

This compound was first prepared by Stadel and Rügheimer (*Ber.*, 1876, **9**, 563), who described it under the name of "isoindol." As subsequently obtained by Stadel and Kleinschmidt (*ibid.*, 1880, **13**, 836), it was observed to exhibit diverse colours, and they regarded it as being "idiochromatic." Pure 2: 5-diphenylpyrazine is, however, quite colourless, as has been shown by Gabriel (*Ber.*, 1908, **41**, 1127), who prepared it by the interaction of ω -bromoacetophenone and ammonia.

The original alcoholic filtrate from the 2: 5-diphenylpyrazine and ammonium chloride was evaporated to a low bulk and largely diluted with benzene. The filtered liquid was then again evaporated as far as possible, and the residue dissolved in alcoholic hydrogen chloride, when the mixture rapidly became dark brown, but no blue colour was developed (see below). The solution was concentrated somewhat, and hot ethyl acetate added, when, on cooling the mixture, a crystalline substance separated in needles, which were collected and washed with a mixture of ethyl acetate and alcoholic hydrogen chloride. The product so obtained was dissolved in the minimum amount of absolute alcohol, and a little alcoholic hydrogen chloride added, when it immediately separated in soft, almost colourless needles, melting at about 189° :

0.2020 gave 0.1060 AgCl. $Cl=13.0$.

$C_{16}H_{12}N_2.HCl$ requires $Cl=13.2$ per cent.

This substance was identified as 2: 6-diphenylpyrazine monohydrochloride,* since it yielded 2: 6-diphenylpyrazine, which formed colourless needles, melting at 90° . (Found, $C=79.3$; $H=5.2$. Calc., $C=79.3$; $H=5.0$ per cent.)

2: 6-Diphenylpyrazine monohydrochloride is almost insoluble in benzene or ethyl acetate, but it dissolves fairly readily in alcohol, owing to the fact that it becomes, for the most part, dissociated. It is not stable in moist air, and is instantly dissociated when brought in contact with water.

Gabriel (*loc. cit.*) did not note the formation of 2: 6-diphenylpyrazine when he investigated the interaction of ω -bromoaceto-

* It has been found that the pyrazines are diacidic bases, and yield two series of salts (compare following paper).

phenone and ammonia, but it would appear certain that it must have been present in the reaction mixture examined by him.

The original filtrate from the 2: 6-diphenylpyrazine hydrochloride was dark brown, and contained considerable resinous matter. It was largely diluted with water, filtered from the precipitated resin, concentrated somewhat, and treated with animal charcoal. On allowing the clear liquid to cool, a somewhat sparingly soluble compound separated, which melted at about 235°, and was subsequently identified as diphenacylamine hydrochloride, a compound which has been described by Gabriel (*loc. cit.*).

In a subsequent preparation of the above-described 2: 5- and 2: 6-diphenylpyrazines, a quantity (40 grams) of ω -chloroacetophenone was heated in an autoclave with an excess of alcoholic ammonia, the mixture being subsequently kept for fourteen days before it was worked up. After separating the ammonium chloride and 2: 5-diphenylpyrazine in the manner already described, the residual solution containing the 2: 6-base, which was of a much more pronounced red colour, and appeared to be free from resinous matter than that obtained in the previous preparation, was mixed with a large volume of ether and extracted several times with a mixture of concentrated hydrochloric acid (1 part) and water (2 parts). This caused the separation of some brown, resinous matter, which was removed. The ethereal liquid was then evaporated, and the red residue dissolved in absolute alcohol, and a solution of hydrogen chloride in the same solvent added. The liquid then became deep blue, and, on cooling the mixture after adding some ethyl acetate, a solid separated, which, when collected, was seen to consist of a mixture of white and deep blue needles, the former predominating. The separation of these two products was tedious, but was eventually effected by taking advantage of the fact that the blue *hydrochloride* was somewhat more sparingly soluble in a boiling solution of hydrogen chloride in absolute alcohol than was the white one, which consisted of 2: 6-diphenylpyrazine hydrochloride. The blue compound crystallised in small needles, which had no definite melting point, and were only stable in dry air or in an anhydrous solvent in the presence of a moderate excess of hydrogen chloride. The amount obtained was only about 0.5 gram, and consequently the formula could not be established:

0.3506 gave 0.4791 AgCl. Cl=33.8 per cent.

The base obtained from this deep blue hydrochloride crystallised from alcohol in small tufts of brilliant scarlet crystals, melting at 195°. It was readily soluble in chloroform, ethyl acetate, or benzene, but only moderately so in alcohol. On exposing a solution of this scarlet-coloured base in chloroform or benzene to direct

sunlight, the colour was discharged in half-an-hour, a compound crystallising in yellow needles being formed.

*Preparation of ω -Chloro-*o*- and *p*-methoxyacetophenones.*

ω -Chloro-*p*-methoxyacetophenone was prepared by Kunckell and Johannssen (*Ber.*, 1897, **30**, 1715; 1898, **31**, 170) by the interaction of anisole and chloroacetyl chloride in the presence of aluminium chloride. Mr. F. W. Caton, who conducted this operation for the present author, found it important to avoid the use of any excess of aluminium chloride and not to employ heat, as the methyl group is very easily eliminated. With the object of avoiding this hydrolysis, experiments were made with the use of sublimed ferric chloride, but the yield of condensed product so obtained was only small.

One molecular proportion of anisole was mixed with rather more than an equivalent amount of chloroacetyl chloride, and, after diluting the mixture with three times its volume of carbon disulphide, one molecular proportion of powdered aluminium chloride was cautiously added, the flask being kept cool during this operation. After three hours the carbon disulphide was decanted, the residue being decomposed with ice and hydrochloric acid and the product extracted with ether. The ethereal liquid was then shaken with aqueous sodium hydroxide, which removed small amounts of hydrolysed product and red resin, after which the solvent was evaporated. On fractionally crystallising the residue from alcohol, it was found to consist, for the most part, of ω -chloro-*p*-methoxyacetophenone (m. p. 102°), which formed long needles, but the more soluble fraction contained a second substance. This compound formed large, colourless, diamond-shaped plates, which, after being separated mechanically from the greater part of the *p*-compound and submitted to several recrystallisations, melted at 69° :

0.2154 gave 0.4571 CO_2 and 0.0993 H_2O . C=57.9; H=5.1.

0.2288 " 0.1778 AgCl . Cl=19.2.

$\text{C}_8\text{H}_9\text{O}_2\text{Cl}$ requires C=58.5; H=4.9; Cl=19.2 per cent.

This substance was evidently ω -chloro-*o*-methoxyacetophenone, since it readily yielded salicylic acid on fusion with potassium hydroxide.

This appears to be the first time that the formation of an *o*-mono-substituted ketone by means of the Friedel and Crafts' reaction has been noted, although phenyl *o*-tolyl ketone has been stated to be formed by the interaction of toluene and benzoic acid in the presence of phosphoric oxide (Kollarits and Merz, *Ber.*, 1873, **6**, 338).

ω -Chloro-*o*-methoxyacetophenone is slightly volatile at the

ordinary temperature, and sublimes readily on heating. It is more volatile in steam than is the corresponding *p*-compound, and may be approximately separated from the latter by taking advantage of this property. When brought into contact with the skin, it causes considerable smarting, and it has an extremely irritant action on the eyes.

Attempts to prepare *o*-methoxydiphenylpyrazines by heating ω -chloro-*o*-methoxyacetophenone with alcoholic ammonia in sealed tubes resulted only in the formation of resinous products.

*ω -Chloro-*o*-hydroxyacetophenone.*

ω -Chloro-*o*-methoxyacetophenone was dissolved in carbon disulphide, one molecular proportion of powdered aluminium chloride added, and the mixture heated for two hours under a reflux condenser. The solvent was then removed, and the residue heated at 100° for ten minutes, after which ice and hydrochloric acid were added, and the product extracted with ether. On shaking the ethereal liquid with a solution of sodium carbonate, nothing was removed, but subsequent treatment with aqueous sodium hydroxide extracted a relatively small proportion of oily matter. The ethereal liquid, on evaporation, yielded a considerable quantity of unchanged ω -chloro-*o*-methoxyacetophenone, this compound being evidently much more stable towards aluminium chloride than is the corresponding *p*-derivative. The oil which had been removed by sodium hydroxide was dissolved in ether, and light petroleum added, which caused the separation of a viscid, red product, whereupon the mixture was shaken with animal charcoal, and filtered. After concentrating the filtrate, a substance separated in yellow, flattened needles, which, after recrystallisation from alcohol, melted at 101°:

0.1238 gave 0.2546 CO₂ and 0.0490 H₂O. C=56.0; H=4.4.

C₈H₇O₂Cl requires C=56.3; H=4.3 per cent.

This substance was therefore ω -chloro-*o*-hydroxyacetophenone, HO·C₆H₄·CO·CH₂Cl. It differed from the corresponding *p*-compound in being insoluble in aqueous sodium carbonate (compare Tutin, Caton, and Hann, *Traus.*, 1909, 95, 2118).

*Interaction of ω -Chloro-*p*-methoxyacetophenone and Ammonia.*

ω -Chloro-*p*-methoxyacetophenone was heated in an autoclave for three hours at 110° with a large excess of alcoholic ammonia. When cool, the solid contained in the dark-coloured reaction mixture was collected and washed, first with alcohol, and subsequently with water. The residue was crystallised from xylene, when it separated in large leaflets, melting at 222°. The substance, as thus obtained,

could not be rendered colourless by recrystallisation, but different preparations of it exhibited diverse tints, such as dull green, purplish, or greenish-yellow. It was, however, rendered colourless by the means previously found useful in the case of 2: 5-diphenylpyrazine (p. 2501), but the melting point was practically unchanged by this treatment. On crystallising the purified substance from glacial acetic acid or xylene, it formed large, colourless leaflets, but when crystallised from chloroform or ethyl acetate it separated in hexagonal plates:

0.1088 gave 0.2947 CO_2 and 0.0556 H_2O . $\text{C}=73.9$; $\text{H}=5.7$.

0.3246 „ 29.0 c.c. N_2 (moist) at 20° and 728 mm. $\text{N}=9.8$.

$\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C}=73.9$; $\text{H}=5.5$; $\text{N}=9.6$ per cent.

A molecular-weight determination by the cryoscopic method gave the following result:

0.3153, in 33.2 of phenol, gave $\Delta t = -0.30^\circ$. M.W. = 243.

$\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$ requires M.W. = 292.

Several attempts were made to estimate the number of methoxyl groups in this substance by Perkin's modification of Zeisel's method, but accurate results could not at first be obtained, owing to the great stability of the compound. It was eventually ascertained, however, that the methyl groups are rapidly eliminated if some glacial acetic acid be added to the hydriodic acid employed:

0.2086 gave 0.3366 AgI. $\text{OMe}=21.1$.

$\text{C}_{16}\text{H}_{10}\text{N}_2(\text{OMe})_2$ requires $\text{OMe}=21.2$ per cent.

The compound was evidently *pp'*-dimethoxy-2: 5-diphenylpyrazine, $\text{C}_{16}\text{H}_{10}\text{N}_2(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, and its constitution was subsequently confirmed by its conversion by hydriodic acid into *o*-amino-*p*-hydroxyacetophenone hydriodide and methyl iodide (p. 2520).

On heating *pp'*-dimethoxy-2: 5-diphenylpyrazine, fusion occurs at 223° , and the substance passes into a "liquid-crystalline" state. This phase persists until a temperature of 265.4° is reached, when the "crystalline" liquid phase instantly passes into the normal liquid state. At the point of change it can easily be observed that the two liquid phases are immiscible, and the "liquid-crystalline" product appears to possess the greater density. The reverse change, from the normal liquid to the "liquid-crystalline" phase, occurs at precisely the same temperature, and is exhibited in a striking manner when viewed through crossed Nicol's prisms. The point of change from the "liquid-crystalline" to the normal liquid phase, and vice versa, of *pp'*-dimethoxy-2: 5-diphenylpyrazine is a much more delicate criterion of the purity of this substance than is its melting point, as a mere trace of impurity causes a very appreciable lowering of the temperature of transition from one liquid phase

to the other, whilst an amount of extraneous substance sufficient to cause a depression of the melting point by about 3° completely extinguishes the "liquid-crystalline" phase.

pp'-Dimethoxy-2:5-diphenylpyrazine is practically insoluble in ether or alcohol, very sparingly soluble in chloroform, benzene, or ethyl acetate, moderately soluble in boiling xylene, and more readily so in glacial acetic acid. Its dilute solution in chloroform exhibits a violet-blue fluorescence, and when a drop of concentrated hydrochloric acid is added, a yellow colour is produced, accompanied by a most brilliant green fluorescence.

The original, dark-coloured, alcoholic filtrate from the ammonium chloride and *pp'*-dimethoxy-2:5-diphenylpyrazine was evaporated to dryness, the residue extracted with benzene, the solution evaporated, and the residue dissolved in absolute alcohol. A solution of hydrogen chloride in absolute alcohol was then added, when, after concentrating the solution, it was mixed with hot ethyl acetate. On cooling the mixture, a compound separated in yellow needles, which were collected, washed with a mixture of alcoholic hydrogen chloride and ethyl acetate, and recrystallised by dissolving them in absolute alcohol, adding alcoholic hydrogen chloride, concentrating the mixture, and then diluting it with ethyl acetate. Soft, yellow needles were thus obtained, which melted at about $178-180^{\circ}$:

0.2420 gave 0.1003 AgCl. Cl=10.3.

$C_{18}H_{16}O_2N_2 \cdot HCl$ requires Cl=10.8 per cent.

This salt proved to be *pp'*-dimethoxy-2:6-diphenylpyrazine monohydrochloride, $C_{18}H_{16}N_2(C_6H_4 \cdot OMe)_2 \cdot HCl$. It dissolves sparingly in ethyl acetate or chloroform containing an excess of hydrogen chloride, but is unstable in moist air, and is dissociated by alcohol or water.

pp'-Dimethoxy-2:6-diphenylpyrazine, $C_{18}H_{16}N_2(C_6H_4 \cdot OMe)_2$, obtained from the above-described salt by treatment with water or alcohol, crystallised from the latter solvent in colourless needles, melting at 137.5° :

0.0987 gave 0.2670 CO_2 and 0.0505 H_2O . C=73.8; H=5.7.

$C_{18}H_{16}O_2N_2$ requires C=73.9; H=5.5 per cent.

pp'-Dimethoxy-2:6-diphenylpyrazine is very readily soluble in chloroform, ethyl acetate, benzene, or xylene, but only moderately so in alcohol. Its neutral solutions exhibit a slight blue fluorescence, but this is destroyed by the addition of concentrated hydrochloric acid. It does not pass into a "liquid-crystalline" state on fusion. The constitution of *pp'*-dimethoxy-2:6-diphenylpyrazine was subsequently proved by its conversion by means of hydriodic acid into

methyl iodide, ammonium iodide, and *pp'*-dihydroxydiphenacylamine hydroiodide (p. 2522).

The filtrate from the crude *pp'*-dimethoxy-2: 6-diphenylpyrazine hydrochloride was dark brown, and contained considerable resinous matter. It was digested with aqueous hydrochloric acid, filtered, and the filtrate treated with animal charcoal. After concentrating the liquid thus obtained, it deposited a relatively small amount of a sparingly soluble hydrochloride. This was recrystallised from water, when it formed leaflets, melting at 256°:

0.2459 gave 0.1003 AgCl. $\text{Cl} = 10.0$.

$\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}_2\text{HCl}$ requires $\text{Cl} = 10.1$ per cent.

This salt was doubtless *pp'*-dimethoxydiphenacylamine hydrochloride, $(\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2)_2\text{NH}_2\text{HCl}$, as it was obtained in a manner analogous to that which resulted in the formation of diphenacylamine hydrochloride from *o*-chloroacetophenone, and its properties are strictly analogous to those of the latter salt. Moreover, from evidence given in the latter part of this communication, it is evident that *pp'*-dimethoxydiphenacylamine must have been formed during the interaction of ammonia and *o*-chloro-*p*-methoxyacetophenone, since the former base is an intermediate compound in the production of the above-described *pp'*-dimethoxy-2: 6-diphenylpyrazine.

It has already been shown in connexion with the preparation of the 2: 5- and 2: 6-diphenylpyrazines that if the reaction mixture were kept for some time before it was worked up, a highly-coloured by-product was formed, together with these bases. This is also the case when working with the *p*-methoxy-derivatives, but in the latter instance several other compounds were also obtained in small amounts, possibly owing to the fact that the reaction mixture was examined much more fully than in the former case.

o-Chloro-*p*-methoxyacetophenone was heated with alcoholic ammonia as above described, but the reaction mixture was kept for three weeks before being examined. The *pp'*-dimethoxy-2: 5-diphenylpyrazine was isolated as before described, but with the use of chloroform instead of xylene. The mother liquors then yielded a small amount of a compound, which formed soft, colourless needles, melting at 232—233°. On working up the original filtrate from the *pp'*-dimethoxy-2: 5-diphenylpyrazine and ammonium chloride in the manner previously described, a mixture of *pp'*-dimethoxy-2: 6-diphenylpyrazine and another salt was obtained. The latter compound was evidently the *p*-methoxy-derivative of the blue hydrochloride previously described; it was dark green, and was separated from the salt of the pyrazine derivative in a manner analogous to that employed in connexion with the previously-

described blue compound. The mother liquors from these hydrochlorides yielded, together with traces of other compounds, a substance which formed yellow leaflets, melting at 213—214°, but did not fluoresce when treated in chloroform solution with hydrochloric acid. The deep green-coloured hydrochloride melted quite indefinitely, owing to dissociation, and this change was also readily brought about by treatment with any solvent which did not contain an excess of anhydrous hydrogen chloride. It yielded a deep crimson-coloured base, crystallising from alcohol in small, lustrous prisms, which were so dark red as to appear almost black, and melted at about 165°. This compound, like the corresponding phenyl derivative previously described, is decolorised by exposure to direct sunlight when dissolved, yielding a yellow substance, which formed needles (m. p. about 255°) from xylene. The amounts of these various by-products obtained was small, and their investigation was not further pursued.

*Derivatives of ω -Amino-*p*-methoxyacetophenone.*

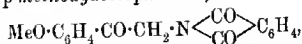
It would appear that the above-described *pp'*-dimethoxy-2:5-di-phenylpyrazine must have been formed by the condensation of two molecules of ω -amino-*p*-methoxyacetophenone, followed by spontaneous oxidation of the resulting *pp'*-dimethoxy-3:6-dihydro-2:5-diphenylpyrazine in a manner analogous to that which has been shown by Gabriel (*loc. cit.*) to result in the formation of 2:5-diphenylpyrazine from ω -aminoacetophenone. With the object, therefore, of verifying this conclusion, ω -amino-*p*-methoxyacetophenone was prepared, in the form of its hydrochloride, as follows.

ω -Chloro-*p*-methoxyacetophenone was heated for some time in a nickel crucible with rather more than one molecular proportion of potassium phthalimide. The reaction mixture was then extracted with boiling xylene, and the product which crystallised from this solvent after concentration was repeatedly boiled with large quantities of water for the removal of unchanged phthalimide. On recrystallising the residue from xylene, glistening leaflets, melting at 164—165°, were obtained:

0.1437 gave 0.3650 CO₂ and 0.0604 H₂O. C = 69.2; H = 4.6.

C₁₇H₁₂O₄N requires C = 69.2; H = 4.4 per cent.

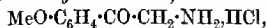
*ω -Phthalimino-*p*-methoxyacetophenone,*



is very sparingly soluble in alcohol, ethyl acetate, or chloroform but dissolves more readily in glacial acetic acid or boiling xylene.

The above-described phthalide derivative was boiled for eight hours with concentrated hydrochloric acid, when it gradually passed

into solution. The mixture was then deprived of phthalic acid by means of ether, and evaporated to dryness under diminished pressure. On crystallising the residue from alcohol, *o*-amino-*p*-methoxyacetophenone hydrochloride,



was obtained in small, colourless prisms, which melted and decomposed at 204° , after having become red:

0.2121 gave 0.1408 AgCl. $\text{Cl} = 16.4$.

$\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl}$ requires $\text{Cl} = 16.6$ per cent.

When an alkali is added to an aqueous solution of *o*-amino-*p*-methoxyacetophenone hydrochloride, no immediate separation of base occurs. The mixture, however, rapidly darkens somewhat, and, after some time, a dark-coloured, semi-crystalline product separates. On purification, this yielded *pp'*-dimethoxy-2:5-diphenylpyrazine (m. p. 223°), thus proving that a change analogous to that observed by Gabriel (*loc. cit.*) had occurred.

o-Amino-*p*-methoxyacetophenone Platinichloride,



—This derivative crystallised very readily in deep yellow leaflets, and melted and decomposed at 225 — 228° :

0.1434 gave 0.0373 Pt. $\text{Pt} = 26.0$.

$(\text{C}_9\text{H}_{11}\text{O}_2\text{N})_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 26.3$ per cent.

o-Amino-*p*-methoxyacetophenone Aurichloride,



The aurichloride did not crystallise readily, but was eventually obtained in handsome, golden-coloured leaflets, which melted at 74° , and evidently contained water of crystallisation:

0.2024 gave 0.0762 Au. $\text{Au} = 37.6$.

$\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot \text{HAuCl}_4 \cdot \text{H}_2\text{O}$ requires $\text{Au} = 37.6$ per cent.

o-Amino-*p*-methoxyacetophenone picrate, $\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, formed small, bright yellow leaflets, which, like the preceding compound, contained water of crystallisation. It melted and decomposed at 185° .

The mercurichloride crystallised very readily in long, colourless needles, which melted at 171° .

o-Chloro-*mp*-dimethoxyacetophenone.

Catechol was methylated by means of methyl sulphate,* and the resulting veratrole purified by distillation. The veratrole was then

* Perkin and Weizmann (Trans., 1906, 89, 1649) state that an almost quantitative yield of veratrole may be obtained by treating 100 grams of catechol with 75 grams of methyl sulphate and 150 grams of potassium hydroxide. The figures

dissolved in carbon disulphide, an equivalent amount of chloroacetyl chloride added, and then one molecular proportion of powdered aluminium chloride introduced. The mixture was heated on a water-bath for two hours, but the reaction which ensued was by no means violent. The carbon disulphide was then removed and the residue decomposed by ice and hydrochloric acid, the product being extracted with ether. On shaking the ethereal liquid with aqueous potassium hydroxide, a small quantity of demethylated product was removed. The ether was then evaporated, and the residue deprived of a fairly large proportion of unchanged veratrole by means of steam. The non-volatile product was crystallised from alcohol, when it yielded *o*-chloro-*mp*-dimethoxyacetophenone, $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Cl}$, which formed small, colourless prisms, melting at 101° :

0.1172 gave 0.2394 CO_2 and 0.0538 H_2O . $\text{C}=55.8$; $\text{H}=5.1$.

$\text{C}_{10}\text{H}_9\text{O}_3\text{Cl}$ requires $\text{C}=55.9$; $\text{H}=5.1$ per cent.

o-Chloro-*mp*-dimethoxyacetophenone is moderately soluble in alcohol, but much more readily so in ethyl acetate or chloroform. When in the dry state, it occasions violent sneezing.

The Interaction of o-Chloro-*mp*-dimethoxyacetophenone and Ammonia.

o-Chloro-*mp*-dimethoxyacetophenone was heated in an autoclave for three hours at 110° with a large excess of absolute alcoholic ammonia. When cool, the solid contained in the reaction mixture was collected, washed with alcohol, and then extracted many times with boiling xylene. The xylene extracts, on cooling, deposited a dark red, crystalline powder, melting at 203° . After treatment with a small amount of potassium permanganate in glacial acetic acid solution, in the manner previously described, it separated from glacial acetic acid in light grey needles, which melted at the same temperature as before this treatment:

0.1130 gave 0.2834 CO_2 and 0.0590 H_2O . $\text{C}=68.4$; $\text{H}=5.8$.

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2$ requires $\text{C}=68.2$; $\text{H}=5.7$ per cent.

This compound was evidently *mm'*/*pp'*-*tetramethoxy-2:5*-diphenylpyrazine, $\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{C}_4\text{H}_2\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OMe})_2$, and its constitution was subsequently confirmed by its conversion into *o*-amino-*mp*-di-hydroxyacetophenone hydriodide and methyl iodide by the action of hydriodic acid (p. 2520). It is insoluble, or nearly so, in all the usual solvents with the exception of glacial acetic acid and boiling xylene, and in the latter solvent it dissolves but sparingly. Its much greater given are, however, obviously incorrect, since the amount of catechol mentioned would require theoretically 229 grams of methyl sulphate and 102 grams of the alkali.

solubility in glacial acetic acid than in any other liquid employed appeared to be due to salt formation, as the solution was orange-yellow, and it was subsequently found that the tetramethoxy-diphenylpyrazines are more strongly basic than the other compounds of this class described in the present communication. A very dilute solution of *mm'*/*pp'*-tetramethoxy-2:5-diphenylpyrazine in chloroform exhibits a strong blue fluorescence, but this phenomenon disappears on the addition of a drop of concentrated hydrochloric acid, a non-fluorescent, deep yellow liquid being produced. On fusion, this pyrazine derivative does not pass into a "liquid-crystalline" state, as is the case with the corresponding *pp'*-dimethoxy compound.

The original alcoholic filtrate from the *mm'*/*pp'*-tetramethoxy-2:5-diphenylpyrazine and ammonium chloride was evaporated to dryness, the residue extracted with benzene, the solution again evaporated, and the product so obtained dissolved in a small amount of absolute alcohol and a solution of hydrogen chloride in the same solvent added. On cooling the dark brown mixture, a compound separated in deep yellow needles. This was collected, washed with alcoholic hydrogen chloride, and recrystallised from absolute alcohol by the addition of a solution of hydrogen chloride in this solvent, when long, deep yellow, soft needles were obtained, which melted at about 195–200°:

0.2030 gave 0.0730 AgCl. $\text{Cl} = 8.9$.

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2\text{HCl}$ requires $\text{Cl} = 9.1$ per cent.

This compound was *mm'*/*pp'*-tetramethoxy-2:6-diphenylpyrazine monohydrochloride, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{C}_4\text{H}_2\text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{HCl}$. It was readily dissociated by water, or by alcohol, unless the latter contained an excess of hydrogen chloride. It yielded *mm'*/*pp'*-tetramethoxy-2:6-diphenylpyrazine, which, when crystallised from alcohol, formed long, almost colourless needles, melting at 160°:

0.1079 gave 0.2734 CO_2 and 0.0563 H_2O . $\text{C} = 68.0$; $\text{H} = 5.8$.

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2$ requires $\text{C} = 68.2$; $\text{H} = 5.7$ per cent.

This base was rather sparingly soluble in alcohol, but readily so in benzene, xylene, chloroform, glacial acetic acid, or ethyl acetate, and differed from the corresponding 2:5-compound, inasmuch as its solutions exhibited no fluorescence. Its constitution was subsequently confirmed by its conversion into *mm'*/*pp'*-tetrahydroxy-diphenacylamine hydriodide, methyl iodide, and ammonium iodide by means of hydriodic acid (p. 2523).

o-Chloro-*op*-dimethoxyacetophenone.

Resorcinol dimethyl ether was prepared from resorcinol by the action of methyl sulphate and potassium hydroxide, and purified by distillation. The dimethyl ether was then dissolved in carbon disulphide, and the requisite amount of chloroacetyl chloride added. One molecular proportion of powdered aluminium chloride was then introduced, when a violent reaction ensued. After removing the solvent, the residue was treated with ice and hydrochloric acid, the resulting solid being collected and crystallised from alcohol. A very good yield of small, colourless, prismatic needles, melting at 96° , was thus obtained:

0.1233 gave 0.2518 CO_2 and 0.0577 H_2O . $\text{C} = 55.7$; $\text{H} = 5.2$.

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{Cl}$ requires $\text{C} = 55.9$; $\text{H} = 5.1$ per cent.

o-Chloro-*op*-dimethoxyacetophenone, $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, is somewhat sparingly soluble in alcohol, but much more readily so in ethyl acetate or chloroform. It was formed in much better yield than the corresponding *mp*-compound.

Attempts to convert *o*-chloro-*op*-dimethoxyacetophenone into pyrazine derivatives by heating with alcoholic ammonia resulted only in the formation of brown resins, just as was the case when *o*-chloro-*o*-methoxyacetophenone was employed. It therefore appears that the presence of a methoxyl group in the ortho-position with respect to the side-chain precludes the formation of substituted pyrazines from *o*-chloroacetophenone derivatives.

Attempts were made to prepare an *o*-chlorotrimethoxyacetophenone by the interaction of chloroacetyl chloride and pyrogallol trimethyl ether, but without success.

o-Amino-*op*-dihydroxyacetophenone and its Derivatives.

It is subsequently shown that the methoxy-2:5-diphenylpyrazines readily yield *o*-aminohydroxyacetophenones, the formation of which was the primary object of this research. Since, however, no pyrazine derivative could be obtained from *o*-chloro-*op*-dimethoxyacetophenone, other means had to be devised for the conversion of this compound into the desired dihydroxy-amine.

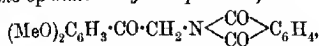
o-Chloro-*op*-dimethoxyacetophenone was heated in a nickel crucible at about 160° with rather more than one molecular proportion of potassium phthalimide until the reaction mixture, which was at first fairly fluid, became almost solid. The product was then extracted several times with boiling xylene, and the combined filtered liquids concentrated to a small bulk. The product which separated on cooling was collected and repeatedly boiled with large

quantities of water until free from phthalimide, after which it was recrystallised from xylene or glacial acetic acid, when it formed acicular crystals, melting at 188°:

0.0903 gave 0.2209 CO₂ and 0.0394 H₂O. C=66.7; H=4.8.

C₁₈H₁₆O₅N requires C=66.5; H=4.6 per cent.

ω-Phthalimino-*o*-dimethoxyacetophenone,



is insoluble, or very sparingly soluble, in all the usual solvents, with the exception of glacial acetic acid and boiling xylene, in which it is moderately soluble.

The above-described phthalide derivative was boiled with concentrated hydriodic acid containing some glacial acetic acid, when it very gradually passed into solution. The mixture was then diluted with water, and repeatedly extracted with ether for the removal of the phthalic acid, after which it was evaporated to dryness under diminished pressure. The solid residue was then dissolved in alcohol, the solution concentrated, ethyl acetate added, and the mixture again evaporated somewhat, when *ω*-amino-*o*-dihydroxyacetophenone hydriodide, C₈H₈(OH)₂·CO·CH₂·NH₂·HI, separated from the boiling mixture:

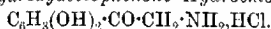
0.2196 gave 0.1733 AgI. I=42.7.

0.4535 „ 0.3405 AgI. I=42.8.

C₈H₈O₃N·HI requires I=43.0 per cent.

ω-Amino-*o*-dihydroxyacetophenone hydriodide forms nearly colourless needles, which decompose at 258°. It is readily soluble in water or alcohol, but dissolves only sparingly in ethyl acetate.

ω-Amino-*o*-dihydroxyacetophenone Hydrochloride,

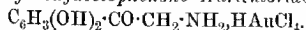


—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide, when the new derivative immediately separated in needles. When crystallised from water or dilute alcohol, it yielded small, hard prisms, which melted at 280°, darkening previously:

0.3297 gave 0.2292 AgCl. Cl=17.2.

C₈H₈O₃N·HCl requires Cl=17.4 per cent.

ω-Amino-*o*-dihydroxyacetophenone Aurichloride,



—The gold salt of *ω*-amino-*o*-dihydroxyacetophenone was readily soluble in water, but crystallised from its concentrated solution in orange-coloured leaflets, which, on heating, gradually darkened, and finally melted at 283°. The dried salt was analysed:

0.1201 gave 0.0467 Au. Au=38.9.

C₈H₈O₃N·HAuCl₄ requires Au=38.9 per cent.

ω-Amino-*op*-dihydroxyacetophenone Platinichloride,

—This derivative was rather readily soluble in water, and crystallised from this solvent in fawn-coloured needles, which melted and decomposed at 247° :

0.1037 gave 0.0294 Pt. Pt=28.5.

$(\text{C}_6\text{H}_3\text{O}_3\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ requires Pt=28.5 per cent.

ω-Amino-*op*-dihydroxyacetophenone picrate, $\text{C}_6\text{H}_3\text{O}_3\text{N} \cdot \text{C}_6\text{H}_3\text{O}_3\text{N}_2$, crystallised from water in bright yellow needles, which melted and decomposed at 222° .

ω-Amino-*op*-dihydroxyacetophenone: $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$ was prepared from the above-described hydride or hydrochloride by the addition of a hot concentrated solution of sodium carbonate to a similar solution of the respective salt, both liquids having previously been deprived of dissolved air by boiling. The new base then immediately separated in small, pink-coloured plates, which, on heating to 310° , suffered some decomposition, but did not melt:

0.1065 gave 0.2240 CO_2 and 0.0558 H_2O . C=57.3; H=5.8.

$\text{C}_6\text{H}_3\text{O}_3\text{N}$ requires C=57.5; H=5.4 per cent.

ω-Amino-*op*-dihydroxyacetophenone is soluble in both acids and alkali hydroxides, but is insoluble, or practically so, in all the usual solvents with the exception of pyridine, although when dissolved in the last-mentioned liquid it suffered change.

Attempts to prepare *ω*-amino-*op*-dimethoxyacetophenone by heating *ω*-phthalimino-*op*-dimethoxyacetophenone with hydrochloric acid were unsuccessful, as the methyl groups were partly eliminated by this treatment, the resulting product being a mixture.

*oo'*pp'-Tetrahydroxy-2:5-diphenylpyrazine.

ω-Amino-*op*-dihydroxyacetophenone was boiled with pyridine, when it slowly dissolved, the solution acquiring a yellow colour. The liquid was then concentrated and cooled, when a substance separated in yellow needles. This was collected, but when washed with ethyl acetate, or when dried, it lost pyridine on crystallisation, and became bright orange-coloured. It was unchanged at 320° , but at a higher temperature sublimed in yellow leaflets:

0.1033 gave 0.2447 CO_2 and 0.0400 H_2O . C=64.6; H=4.3.

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2$ requires C=64.8; H=4.1 per cent.

This substance was evidently *oo'*pp'-tetrahydroxy-2:5-diphenylpyrazine, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{C}_7\text{H}_2\text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$, and had been formed by the condensation of two molecules of the original keto-base followed by spontaneous oxidation of the resulting *oo'*pp'-tetrahydroxy

3-6-*dihydro*-2:5-*diphenylpyrazine*. It yielded unstable salts with the mineral acids, of which the *monosulphate* was bright orange and the *disulphate* intense purple. *oo'pp'*-Tetrahydroxy-2:5-diphenylpyrazine is very sparingly soluble in glacial acetic acid, more readily soluble in pyridine, and insoluble in all the other usual solvents.

oo'pp'-Tetrahydroxy-2:5-*diphenylpyrazine*,
 $C_6H_3(OBz)_2 \cdot C_4H_2N_2 \cdot C_6H_3(OBz)_2$.

—The above-described *oo'pp'*-tetrahydroxy-2:5-diphenylpyrazine readily underwent benzylation when treated according to the Schotten-Baumann method, yielding a product which crystallised from ethyl acetate in glistening, colourless leaflets, melting at 212° :

0.0976 gave 0.2643 CO_2 and 0.0356 H_2O . $C=73.8$; $H=4.0$.

$C_{44}H_{28}O_8N_2$ requires $C=74.1$; $H=3.9$ per cent.

oo'pp'-Tetrahydroxy-2:5-*diphenylpyrazine* is somewhat sparingly soluble in ethyl acetate and in alcohol, but dissolves readily in chloroform.

With the object of preparing the benzoyl derivative of *o*-amino-*p*-dihydroxyacetophenone, the hydriodide of this base was dissolved in water, benzoyl chloride added, and then excess of aqueous potassium hydroxide introduced, and the mixture shaken for some time. The pasty product which separated was collected, dissolved in boiling absolute alcohol, and then submitted to steam distillation for the removal of the ethyl benzoate which had been formed from the occluded excess of benzoyl chloride. The non-volatile residue was dissolved in alcohol, when, on keeping, a crystalline benzoyl derivative separated, but by no means in quantitative yield. The mother liquors from this solid contained an uncrystallisable oil, which, from a subsequent observation, would appear to have been the compound which it was sought to prepare, namely, *o*-benzoylamino-*op*-dibenzoyl-acetophenone, $C_6H_3(OBz)_2 \cdot CO \cdot CH_2 \cdot NHBz$. The crystalline solid which was obtained formed small prisms, melting at $136-137^\circ$, and, on analysis, was found to be the benzoyl derivative of a condensation product of the base:*

0.1532 gave 0.4106 CO_2 and 0.0624 H_2O . $C=73.1$; $H=4.5$.

$C_{22}H_{15}O_4N$ requires $C=73.6$; $H=4.2$ per cent.

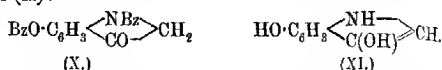
0.2970, in 24 of benzene, gave $\Delta t = -0.165^\circ$. M.W. = 375.

$C_{22}H_{15}O_4N$ requires M.W. = 357.

This compound was therefore the dibenzoyl derivative of an internal anhydride of *o*-amino-*op*-dihydroxyacetophenone, and since an analogous compound was obtained from *o*-amino-*o*-hydroxyacetophenone (p. 2518), but not from the related bases containing

* The same compound was obtained when *o*-amino-*op*-dihydroxyacetophenone hydriodide was benzyolated in pyridine solution.

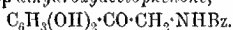
hydroxyl groups in the *m*- or *p*-positions, it would seem likely that the *o*-hydroxyl group was concerned in the anhydride formation. In view of this consideration, it would appear probable that the substance melting at 136–137° is a dibenzoyl derivative of 6-hydroxyindoxyl (X):



6-Hydroxyindoxyl, however, might have been expected to react in its enolic form (XI), yielding a tribenzoyl derivative.

That one of the benzoyl groups was attached to nitrogen was proved by the conversion of this dibenzoyl derivative into *o*-benzoylamino-*op*-dihydroxyacetophenone by the action of alkali hydroxides.

o-Benzoylamino-*op*-dihydroxyacetophenone,



—A quantity of the dibenzoyl derivative melting at 136–137° was boiled with concentrated alcoholic potassium hydroxide for one hour, when water was added, and the mixture acidified with hydrochloric acid. A compound then separated in slender, glistening prisms, melting and decomposing at 260–265°:

0.1339 gave 0.3267 CO₂ and 0.0590 H₂O. C=66.5; H=4.8.

C₁₅H₁₃O₄N requires C=66.4; H=4.8 per cent.

o-Benzoylamino-*op*-dihydroxyacetophenone is very sparingly soluble in alcohol, ethyl acetate, chloroform, or benzene, moderately so in glacial acetic acid, and readily so in pyridine. On prolonged heating with concentrated hydrochloric acid, it yielded *o*-amino-*op*-dihydroxyacetophenone hydrochloride and benzoic acid, and on benzoylation it yielded a compound which appeared to be the tribenzoyl derivative of the corresponding base. This compound was a liquid, and was doubtless identical with the similar product which was obtained together with the dibenzoyl derivative melting at 136–137°, as previously noted.

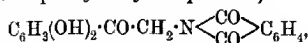
o-Phthalimino-*op*-dihydroxyacetophenone.

During the hydrolysis of *o*-phthalimino-*op*-dimethoxyacetophenone by means of hydriodic acid, it was observed that the reaction proceeded in two stages, the methyl groups being much more rapidly eliminated than was the phthalyl radicle. In one experiment therefore, the reaction was stopped as soon as the evolution of methyl iodide had ceased, the mixture being diluted with water and cooled. A solid then separated, which was collected and washed. When recrystallised from acetic acid, this substance formed small tufts of short, colourless prisms, which gradually darkened above 250°, and fused at 270°:

0.1835 gave 0.4350 CO₂ and 0.0637 H₂O. C=64.6; H=3.8.

C₁₆H₁₁O₅N requires C=64.6; H=3.7 per cent.

ω-Phthalimino-*op*-dihydroxyacetophenone,



is rather sparingly soluble in most solvents. When heated with concentrated hydrochloric or hydriodic acids, it yielded the corresponding amine.

ω-Phthalimino-*op*-dihydroxyacetophenone,



The above-described phthalimino-derivative was dissolved in aqueous potassium hydroxide, and the solution boiled for some time. The mixture was then acidified with hydrochloric acid, boiled with animal charcoal, and the filtered liquid concentrated to a small bulk and cooled. The solid which separated consisted largely of potassium chloride, but also contained crystals of an organic compound. The latter was isolated by extraction with boiling xylene, after which it was finally purified by crystallisation from water. Long, glistening leaflets were thus obtained, which melted at 227°:

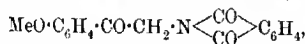
0.1372 gave 0.3064 CO₂ and 0.0519 H₂O. C=60.9; H=4.2.

C₁₆H₁₃O₆N requires C=61.0; H=4.1 per cent.

Derivatives of *ω*-Amino-*o*-hydroxyacetophenone.

Since *ω*-chloro-*o*-methoxyacetophenone gave only resinous products when heated with ammonia, it was necessary to employ potassium phthalimide for the conversion of this chloro-ketone into the corresponding amine, just as was the case with the analogous *op*-dimethoxy-compound (compare p. 2512).

ω-Chloro-*o*-methoxyacetophenone was therefore converted into the corresponding phthalimino-derivative in a manner precisely similar to that employed in the case of the *op*-dimethoxy-derivative. The resulting *ω*-phthalimino-*o*-methoxyacetophenone,



is very sparingly soluble in most solvents, but was readily purified by crystallisation from slightly diluted acetic acid. It formed colourless, diamond-shaped plates, melting at 200.5°:

0.1553 gave 0.3972 CO₂ and 0.0632 H₂O. C=69.5; H=4.5.

C₁₇H₁₅O₄N requires C=69.2; H=4.4 per cent.

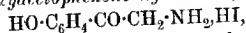
This derivative was boiled for three hours with a mixture ofacial acetic acid and concentrated hydriodic acid. After freeing the liquid from phthalic acid by extraction with ether, the mixture was evaporated to dryness under diminished pressure, and the residue crystallised from a mixture of ethyl acetate and alcohol.

Very lustrous, colourless plates were thus obtained, which melted at 255° :

0.3846 gave 0.3230 AgI. $I = 45.4$.

$C_8H_9O_2N, HI$ requires $I = 45.5$ per cent.

o-Amino-*o*-hydroxyacetophenone hydriodide,



is very readily soluble in water or alcohol, but only sparingly so in ethyl acetate. It does not tend to become discoloured, as is the case with salts of the analogous bases containing a hydroxyl group in the meta- or para-position with respect to the side-chain.

A quantity of this hydriodide was dissolved in pyridine and benzoylated by means of benzoyl chloride. The product crystallised readily from ethyl acetate, forming colourless plates, which melted at 133° :

0.1277 gave 0.3538 CO_2 and 0.0530 H_2O . $C = 75.6$; $H = 4.6$.

$C_{15}H_{11}O_2N$ requires $C = 75.9$; $H = 4.7$ per cent.

This compound was therefore evidently the benzoyl derivative of a condensation product of *o*-amino-*o*-hydroxyacetophenone, and is doubtless constituted analogously to the corresponding derivative of the *op*-dihydroxy-base (p. 2516). It may therefore be 1-benzoyl-indoryl, a compound which does not appear to have been prepared previously.

oo'-Dihydroxy-2:5-diphenylpyrazine.

A quantity of *o*-amino-*o*-hydroxyacetophenone hydriodide was dissolved in water and aqueous sodium carbonate added, the resulting precipitate being collected, and crystallised from xylene. A substance was thus obtained in yellow needles, which melted at $259-262^{\circ}$, and were insoluble in dilute acids. The same compound was obtained if the solution of the hydriodide were rendered alkaline by means of sodium hydroxide, and then acidified, the resulting precipitate being recrystallised from xylene:

0.0904 gave 0.2420 CO_2 and 0.0400 H_2O . $C = 73.0$; $H = 4.9$.

$C_{16}H_{12}O_2N_2$ requires $C = 72.7$; $H = 4.5$ per cent.

This substance was evidently a condensation product, and its properties indicated it to be *oo'*-dihydroxy-2:5-diphenylpyrazine. $C_4H_2N_2(C_6H_4 \cdot OH)_2$. It is very sparingly soluble or insoluble in nearly all solvents, and forms unstable salts of a bright red colour when treated with mineral acids in an anhydrous solvent. When heated above its melting point, it sublimed in yellow leaflets.

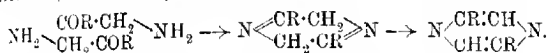
It appears from this result that *o*-amino-*o*-hydroxyacetophenone, when dissolved, behaves in a manner strictly analogous to that exhibited by the *op*-dihydroxy-base. That is to say, that two molecules condense with the formation of *oo'*-dihydroxy-3:6-di-

hydro-2: 5-diphenylpyrazine, which then undergoes spontaneous oxidation to the corresponding pyrazine derivative.

oo'-Dibenzoyloxy-2: 5-diphenylpyrazine, $C_{14}H_{12}N_2(C_6H_5 \cdot OBz)_2$, was prepared by benzoylating the above-described pyrazine derivative in pyridine solution. It formed small, almost colourless prisms, which melted at 185° , but the amount available was not sufficient for analysis.

Action of Hydriodic Acid on pp'-Dimethoxy-2: 5-diphenylpyrazine.

As previously shown, the methoxy-2: 5-diphenylpyrazines described in the present paper, which contain the substituent ether groupings in the meta- and para-positions, are formed by the condensation of two molecules of an ω -aminomethoxyacetophenone, followed by spontaneous oxidation of the resulting dihydropyrazine derivative, as follows (Gabriel, *loc. cit.*):



The corresponding ω -aminohydroxyacetophenones, however, could not be caused to condense under any conditions.

This behaviour is the reverse of that shown by the ortho-substituted ω -aminoacetophenones, for ω -amino-*o*-methoxyacetophenone and ω -amino-*op*-dimethoxyacetophenone will not yield pyrazines, whilst the corresponding hydroxy-derivatives spontaneously pass into such compounds.

With the object therefore of preparing *pp'*-dihydroxy-2: 5-diphenylpyrazine, the action of hydriodic acid on *pp'*-dimethoxy-2: 5-diphenylpyrazine was investigated. It was found, however, that this acid alone had only an extremely slow action on the compound in question, but that if a quantity of acetic acid were added to the mixture, a change ensued with moderate rapidity. The product obtained, however, was not the expected hydroxy-diphenylpyrazine, but the reaction proceeded further, fission of the pyrazine nucleus taking place, resulting in the formation of two molecules of ω -amino-*p*-hydroxyacetophenone (Tutin, Caton, and Iann, *loc. cit.*). It was thus shown that the series of reactions which result in the formation of pyrazine derivatives from ω -aminoacetophenones can be quantitatively reversed by means of hydriodic acid.

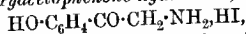
A quantity of *pp'*-dimethoxy-2: 5-diphenylpyrazine was boiled for 50 hours with a mixture of concentrated hydriodic and glacial acetic acids. The liquid was then diluted with water and extracted with ether for the removal of iodine, after which it was evaporated dryness under diminished pressure. On crystallising the residue

from ethyl acetate, colourless, prismatic needles were obtained, which melted at 230°:

0.3435 gave 0.2885 AgI. $I=45.4$.

$C_8H_9O_2N.HI$ requires $I=45.5$ per cent.

ω-Amino-*p*-hydroxyacetophenone hydriodide,



is much more soluble in organic solvents than is the corresponding hydrochloride (Tutin, Caton, and Hann, *loc. cit.*). On benzoylation, it yielded *ω*-benzoylamino-*p*-benzoyloxyacetophenone, melting at 173–174°.

Action of Hydriodic Acid on mm'pp'-Tetramethoxy-2:5-diphenylpyrazine.

mm'pp'-Tetramethoxy-2:5-diphenylpyrazine was boiled for two hours with a mixture of glacial acetic and concentrated hydriodic acids, after which the liquid was diluted, extracted with ether, and evaporated to dryness under diminished pressure. The residue was crystallised from a mixture of ethyl acetate and alcohol, when it formed small, nearly colourless prisms, melting at 247–248°:

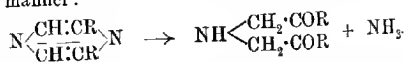
0.2175 gave 0.1717 AgI. $I=42.7$.

$C_8H_9O_3N.HI$ requires $I=43.0$ per cent.

This salt was therefore evidently *ω*-amino-*mp*-dihydroxyacetophenone hydriodide, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot NH_2, HI$. On rendering its solution alkaline with sodium carbonate, *ω*-amino-*mp*-dihydroxyacetophenone separated in nearly colourless leaflets, which gradually decomposed and melted above 235°. This base has previously been prepared by another method during the synthesis of epinephrine (D.R.-P. 155632), and the above-described reaction therefore affords a new means of obtaining this important compound.

Action of Hydriodic Acid on 2:6-Diphenylpyrazine.

As the action of hydriodic acid on the 2:5-substituted pyrazines was found to result in the complete disruption of the pyrazine ring it was considered of interest to investigate the effect of this reagent on the analogous 2:6-substituted bases. It was then found that the nitrogen-containing ring was broken in this case also, in the following manner:



A quantity of 2:6-diphenylpyrazine was heated for several hours with a mixture of concentrated hydriodic and glacial acetic acid. On allowing the liquid to cool, a sparingly soluble hydriodide separated. This was collected, and recrystallised from glacial acetic acid.

acid, when it formed flattened needles, which melted and decomposed at 211° . This salt proved to be *diphenacylamine hydriodide*, $(C_6H_5 \cdot CO \cdot CH_2)_2NH, HI$:

0.1981 gave 0.1217 AgI. $I = 33.2$.

$C_{16}H_{16}O_2N, HI$ requires $I = 33.3$ per cent.

This hydriodide was converted into the corresponding hydrochloride by treatment with hydrochloric acid in alcoholic solution, when glistening leaflets were obtained, which melted at 235° , after previously becoming red. (Found, $Cl = 12.4$. Calc., $Cl = 12.3$ per cent.) This salt had all the properties of diphenacylamine hydrochloride, as described by Gabriel (*loc. cit.*), and it yielded gold and platinum salts, in agreement with the similar derivatives prepared by him.

The original acid filtrate from the diphenacylamine hydriodide was evaporated to dryness under diminished pressure, and the residue crystallised from a mixture of ethyl acetate and alcohol. A colourless salt was thus obtained, which dissolved easily in water, and was readily recognised by the usual tests as ammonium iodide.

Conversion of Diphenacylamine into 2:6-Diphenylpyrazine.

Both Gabriel (*loc. cit.*) and the present author (p. 2502) have obtained diphenacylamine by the interaction of *o*-bromo- or chloroacetophenone and ammonia, and the present author has shown that 2:6-diphenylpyrazine is also formed in this reaction (p. 2501). Now, since diphenacylamine results when this pyrazine derivative is heated with hydriodic acid, it appeared to the present author that the former base might be the intermediate compound in the formation of the latter by the reaction mentioned. This has been found to be the case, for, when one of the above-described salts of diphenacylamine was heated with ammonia, 2:6-diphenylpyrazine was regenerated. It is thus seen that the change which results in the formation of 2:6-diphenylpyrazine is capable of reversion by means of hydriodic acid, just as has been shown to be the case with the analogous 2:5-substituted pyrazines.

A quantity of diphenacylamine hydrochloride was heated in a sealed tube for three hours at 100° with a large excess of a solution of ammonia in absolute alcohol. The reaction mixture was then evaporated to dryness, the residue extracted with benzene, and the benzene liquids evaporated. The dark-coloured residue so obtained was dissolved in a small amount of ethyl acetate, and a solution of hydrogen chloride in absolute alcohol added, when 2:6-diphenylpyrazine monohydrochloride (m. p. 189°) separated. On treatment with alcohol, this salt dissociated, yielding 2:6-diphenylpyrazine, melting at 90° .

It is, of course, evident that the interaction of diphenacylamine and ammonia must first result in the formation of a dihydro-2:6-diphenylpyrazine, the latter then undergoing spontaneous oxidation.

Action of Hydriodic Acid on pp'-Dimethoxy-2:6-diphenylpyrazine.

A quantity of *pp'*-dimethoxy-2:6-diphenylpyrazine was boiled for several hours with a mixture of concentrated hydriodic and glacial acetic acids. On allowing the mixture to cool, a very sparingly soluble hydriodide separated in long, colourless needles, which melted and decomposed at 251° :

0.1050 gave 0.1805 CO_2 and 0.0392 H_2O . $\text{C}=46.8$; $\text{H}=4.1$.

$\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{HI}$ requires $\text{C}=46.5$; $\text{H}=3.8$ per cent.

This salt therefore was *pp'*-dihydroxydiphenacylamine hydriodide, $(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{NHI}$. It was very sparingly soluble in water, and rather more soluble in alcohol, but was insoluble in cold solvents in the presence of an excess of hydriodic acid. *pp'*-*di*-hydroxydiphenacylamine, prepared from this salt, formed dark red crystals, but as it was very unstable it was not further investigated.

pp'-Dihydroxydiphenacylamine Hydrochloride,

$(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}\cdot\text{HCl}$.

—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide. It crystallised from alcohol in colourless leaflets, or from water in needles, and melted at 279° . It is less soluble in alcohol than the hydriodide, but dissolves in water more readily than the latter:

0.2093 gave 0.0914 AgCl . $\text{Cl}=10.8$.

$\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{HCl}$ requires $\text{Cl}=11.0$ per cent.

pp'-Dihydroxydiphenacylamine Platinichloride,

$[(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}]_2\text{H}_2\text{PtCl}_6$.

—This derivative crystallised very readily in buff-coloured needles which melted and decomposed at 230° :

0.1210 gave 0.0241 Pt . $\text{Pt}=19.9$.

$(\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2)_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=19.9$ per cent.

pp'-Dihydroxydiphenacylamine Aurichloride,

$(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}\cdot\text{HAuCl}_4$.

—This salt crystallised readily in bright yellow needles, which melted at 259° after undergoing some decomposition:

0.1012 gave 0.0319 Au . $\text{Au}=31.5$.

$\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{HAuCl}_4$ requires $\text{Au}=31.5$ per cent.

pp'-*Dihydroxydiphenacylamine picrate*, $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_7$, forms long, bright yellow needles, which melt at 169° .

Conversion of pp'-Dihydroxydiphenacylamine into pp'-Dihydroxy-2: 6-diphenylpyrazine.

pp'-Dihydroxydiphenacylamine hydrochloride was heated for two hours in a sealed tube at 100° with a large excess of a solution of ammonia in absolute alcohol. The mixture was then evaporated, and the residue extracted with boiling xylene. On crystallising from glacial acetic acid the material dissolved by the xylene, small, pale yellow prisms, melting at 305°, were obtained:

0.1210 gave 0.3192 CO₂ and 0.0496 H₂O. C=72.5; H=4.5.

C₁₆H₁₂O₂N₂ requires C=72.7; H=4.5 per cent.

This compound was evidently pp'-dihydroxy-2: 6-diphenylpyrazine, C₁₆H₁₂N₂(C₆H₄·OH)₂. It yielded unstable salts with the mineral acids, the monohydrochloride and monosulphate being orange-coloured, whilst the disulphate was deep reddish-purple.

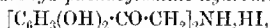
Action of Hydriodic Acid on mm'pp'-Tetramethoxy-2: 6-diphenylpyrazine.

mm'pp'-Tetramethoxy-2: 6-diphenylpyrazine was heated with hydriodic acid in a manner similar to that described in connexion with the corresponding dimethoxy-compound. A hydriodide was thus obtained, which crystallised from acetic acid in colourless leaflets, and melted and decomposed at 236°:

0.1725 gave 0.0918 AgI. I=28.3.

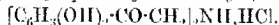
C₁₆H₁₃O₆N₂·HI requires I=28.5 per cent.

mm'pp'-Tetrahydroxydiphenacylamine hydriodide,



is somewhat more soluble in water than the corresponding dihydroxy-compound. On treating its aqueous solution with alkalis, a yellow colour is produced, but oxidation very rapidly ensues, with the development of a brown colour.

mm'pp'-Tetrahydroxydiphenacylamine Hydrochloride,



—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the above-described hydriodide, when the new derivative immediately separated. It crystallises from water in colourless leaflets, which melt and decompose at 264°:

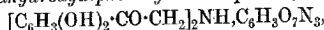
0.2687 gave 0.1075 AgCl. Cl=9.9.

C₁₆H₁₃O₆N₂·HCl requires Cl=10.0 per cent.

On treating a solution of mm'pp'-tetrahydroxydiphenacylamine hydrochloride with auric or platinum chloride, the respective metal was quickly deposited. A mercurichloride was obtained from the

hydrochloride in tufts of small, white needles, but it was unstable, and, on warming its solution, mercurous chloride soon separated.

*mm'*pp'-Tetrahydroxydiphenacylamine picrate,



crystallised readily in tufts of yellow needles, which contained water of crystallisation, and, when air dried, melted at $112\text{--}115^\circ$.

In conclusion, the author wishes to acknowledge his indebtedness to Mr. F. W. Caton, B.A., B.Sc., for the preparation and purification of the *o*-chloro-*o*- and *p*-methoxyacetophenones employed in this research.

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CCLVIII.—*The Absorption Spectra of Some Substituted Pyrazines and their Salts.*

By FRANK TUTIN and FREDERIC WILLIAM CATON.

In the preceding paper, the preparation of 2: 5- and 2: 6-diphenylpyrazine, *pp'*-dimethoxy-2: 5- and -2: 6-diphenylpyrazine, and *mm'*pp'-tetramethoxy-2: 5- and -2: 6-diphenylpyrazine is described. During the course of this work, certain remarkable colour changes were observed on treating these bases with acids, which suggested to us that a fuller investigation of the subject might lead to interesting results. Thus, whilst the hydrochloride of 2: 6-diphenylpyrazine appeared colourless, the corresponding salts of the analogous *pp'*-dimethoxy- and *mm'*pp'-tetramethoxy-bases were bright yellow and orange-coloured respectively. Furthermore, on adding sulphuric acid to a chloroform solution of *pp'*-dimethoxy-2: 5-diphenylpyrazine, a yellow liquid which exhibited an intense, green fluorescence was first produced, whilst on the addition of an excess of the acid a very deep violet-coloured solution resulted.

The further investigation of the bases in question rendered it evident that pyrazine derivatives, which have hitherto been stated to be monoacidic bases, in reality yield two series of salts, the di-acid salts being in all cases much more highly coloured than the corresponding derivatives containing but one equivalent of acid. The depth of colour of corresponding salts of analogous bases was found to increase with the accumulation of methoxyl groups, and to be somewhat greater in compounds of the 2: 5-series than in the corresponding members of the 2: 6-series.

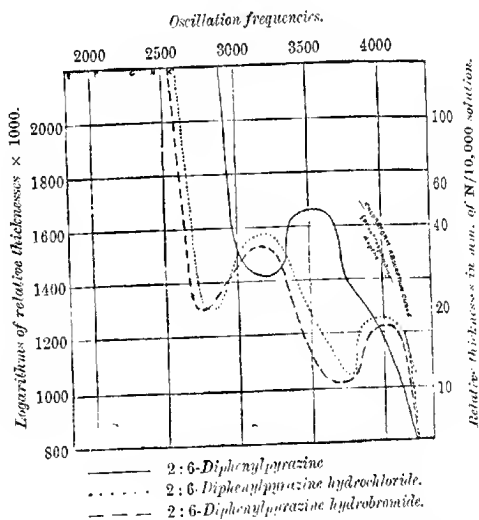
The colours of the salts obtained will be seen on reference to the following table:

| Base. | Mono-hydrochloride. | Mono-hydroxide. | Mono-phosphate. | Dihydrochloride. | Disulphate. |
|--|----------------------------------|---------------------------|-----------------------|-------------------------|--|
| 2:5-Diphenylpyrazine. | Very pale yellow solution. | Pale yellow solution. | (?) | Bright yellow solution. | Yellow crystals. |
| 2:6-Diphenylpyrazine. | Practically colourless crystals. | Pale yellow crystals. | Colourless crystals. | Yellow solution. | Yellow crystals. |
| 2 <i>pp'</i> -Dimethoxy-2:5-diphenylpyrazine. | Bright yellow crystals. | Orange-coloured crystals. | Yellow crystals. | (?) | Yellow solution. |
| 2 <i>pp'</i> -Dimethoxy-2:6-diphenylpyrazine. | Yellow crystals. | Deep yellow crystals. | Pale yellow crystals. | (Could not be formed.) | Crystals resuming potassium permanganate. |
| 2 <i>mm'</i> -Tetramethoxy-2:6-diphenylpyrazine. | Deep yellow crystals. | Orange-coloured crystals. | Yellow crystals. | (Could not be formed.) | Violet-coloured solution. |
| | | | | | Deep blue solution or black crystals with metallic lustre. |
| | | | | | Deep blue solution. |

In order therefore to throw some light on the nature of the colour changes, some of the above-mentioned bases and certain of their salts have been examined spectroscopically in chloroform solution. This solvent was chosen as both the bases and their salts are sufficiently soluble in it, and, although it has a certain amount of general absorption in the extreme ultra-violet region of the spectrum, it was thought that it would not interfere appreciably with the results. Moreover, the salts of the pyrazines have much less tendency to hydrolyse when dissolved in chloroform than in alcoholic solution.*

The curves obtained from 2:6-diphenylpyrazine, *pp'*-dimethoxy-

FIG. 1.



2:6-diphenylpyrazine, and *mm'pp'*-tetramethoxy-2:6-diphenylpyrazine are shown in Figs. 1, 2, and 3 respectively. From these it is seen that each of the bases shows absorption in the ultra-violet part of the spectrum, and that salt-formation is accompanied by a considerable shift of the bands towards the red end, thus accounting for the development of colour on treatment with acids. In the case of 2:6-diphenylpyrazine hydrochloride, which is practically colourless, the absorption bands still lie within the ultra-violet.

* Even when employing chloroform as a solvent for the salts it was necessary to have a certain excess of the respective acid in the solution.

FIG. 2.

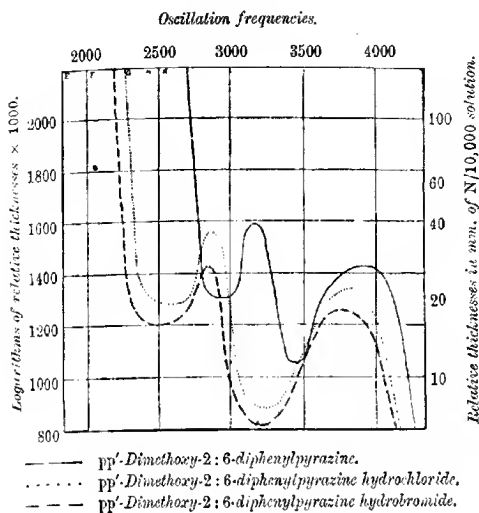
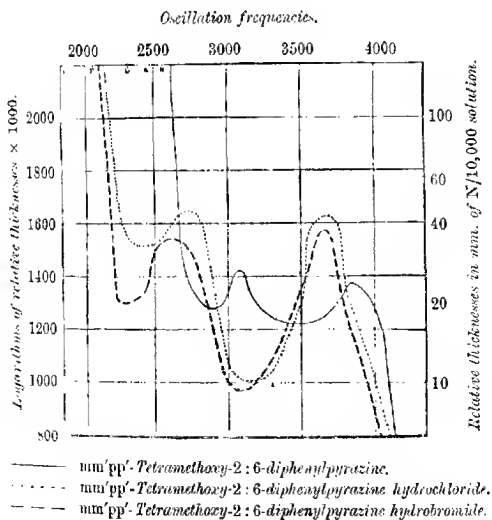
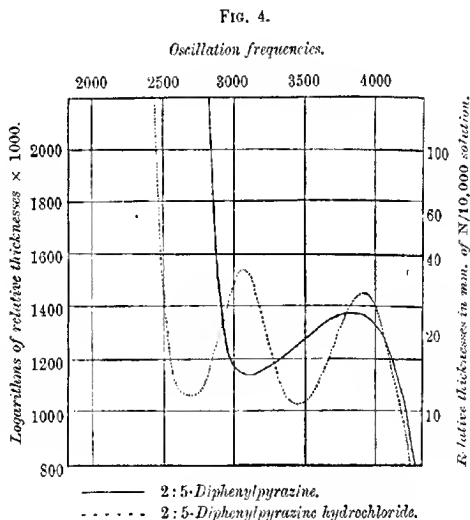


FIG. 3.



region, but one band shown by the corresponding hydrobromide just extends into the visible part of the spectrum, thus explaining the pale yellow colour of the salt in question. The shift of the absorption bands towards the red end of the spectrum caused by the substitution of hydrobromic for hydrochloric acid is not nearly so great as that caused by the conversion of the base into its hydrochloride, thus indicating that the alteration in position of the bands in the latter case must be due chiefly to salt-formation, and only in a minor degree to the weight or nature of the acid radicle attached.

The di- and tetra-methoxy-bases of the 2: 6-series, and all of the salts show two absorption bands, but in the case of 2: 6-diphenyl-



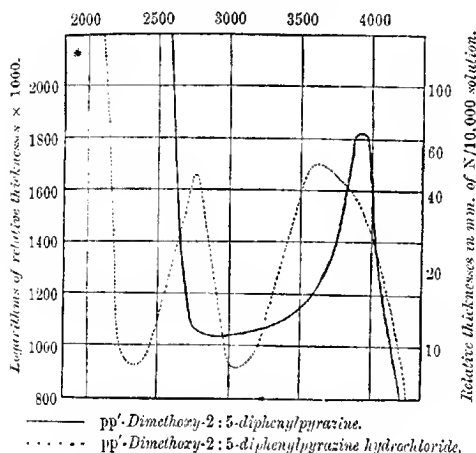
pyrazine only one band is seen. Nevertheless, it is considered most probable that the absorption of all three 2: 6-substituted bases is, in reality, similar, the second absorption band of the last-mentioned base being lost owing to the absorption shown by the chloroform which was used as a solvent.

The curves yielded by 2: 5-diphenylpyrazine and its monohydrochloride, and by *pp'*-dimethoxy-2: 5-diphenylpyrazine and the corresponding salt of this base, are shown in Figs. 4 and 5 respectively. It will be observed in the case of these 2: 5-substituted bases that the curves show only one absorption band, whilst two such are exhibited by the curves obtained from the salts. One possible

explanation of this is that the second absorption band of the 2:5-substituted bases has been lost owing to the absorption caused by the chloroform, just as is thought likely to be the case with 2:6-diphenylpyrazine, as already mentioned. On the other hand, the fact that the band shown by the 2:5-substituted bases is much broader than either of the bands in any of the other curves obtained would suggest that in the bases of the 2:5-series the two absorption bands may have become merged into one.

Certain general conclusions may be drawn from the absorption curves given, namely, the following: (1) The similarity of the

FIG. 5.
Oscillation frequencies.



curves given by the bases and their salts, particularly in the 2:6-series, indicates that no change other than the rearrangement of valencies necessitated by the change $N^{III} \rightarrow N^I$ occurs on treating the bases in question with acids. (2) That salt-formation causes an increased persistency of the bands, together with a very large shift towards the red end of the spectrum. This result is similar to, but very much greater than, that which has previously been observed in the case of pyridine and its homologues (Hartley, *Trans.*, 1885, **47**, 685; Baker and Baly, *ibid.*, 1907, **91**, 1122; and Purvis, *Proc. Camb. Phil. Soc.*, 1908, **14**, 436). (3) The introduction of methoxyl groups causes a shift of the absorption bands towards the red end of the spectrum—an effect which has several times pro-

viously been noted by other workers. (4) The position of the substituent groups in the pyrazine nucleus affects the position of the absorption bands shown by the bases and their salts, the bands shown by the 2:5-substituted compounds being nearer the red end of the spectrum than those shown by their 2:6-substituted isomerides (compare Purvis, *loc. cit.*).

The absorption curves given also appear to indicate that the weight of the acid radical present in a given salt had an effect on the position of the bands, the hydrobromides being more deeply coloured than the corresponding hydrochlorides. It would appear premature, however, to consider this conclusion as proved, without considerable further evidence obtained by the study of a variety of salts, for, in every case where the sulphates could be obtained, they were found to be less deeply coloured than even the corresponding hydrochlorides, but their absorption spectra were not examined. It thus appears that the nature of the acid employed may have a greater effect than its molecular weight on the colour of the resulting salt.

The formation and properties of the salts which were obtained from the pyrazine derivatives under consideration are described below. In most cases the melting points of these derivatives were indefinite, and of no value for the purpose of characterisation.

Salts of 2:5-Diphenylpyrazine.—No salt of this base with one equivalent of an acid could be obtained in the solid state, but the *dihydrobromide* and *disulphate* crystallised readily. On passing hydrogen chloride into a chloroform solution of the base, a yellow liquid was obtained, which doubtless contained the *dihydrochloride*.

Dry hydrogen bromide was passed into a solution of 2:5-diphenylpyrazine in glacial acetic acid, and the mixture kept a few hours. Golden-yellow crystals then separated, which were found to be 2:5-diphenylpyrazine dihydrobromide, $C_{16}H_{12}N_2(C_6H_5)_2 \cdot 2HBr$:

0.1527 gave 0.1435 AgBr. $HBr = 40.5$.

$C_{16}H_{12}N_2 \cdot 2HBr$ requires $HBr = 41.1$ per cent.

This salt was readily dissociated by water, alcohol, or moist air. On heating it with ethyl acetate, it dissolved and partly dissociated, and, on cooling the solution, a mixture of dihydrobromide and base separated, but no monohydrobromide was obtained.

2:5-Diphenylpyrazine disulphate, $C_{16}H_{12}N_2(C_6H_5)_2 \cdot 2H_2SO_4$, resulted on the addition of concentrated sulphuric acid to a solution of the respective base in ethyl acetate or glacial acetic acid; the monosulphate could not be obtained. 2:5-Diphenylpyrazine disulphate forms yellow plates, which, when exposed to moist air, readily dissociate, yielding the colourless base:

0.2117 gave 0.2570 BaSO_4 . $\text{H}_2\text{SO}_4 = 44.7$.

$\text{C}_{16}\text{H}_{12}\text{N}_2 \cdot 2\text{H}_2\text{SO}_4$ requires $\text{H}_2\text{SO}_4 = 45.8$ per cent.

Although the result of this analysis is not in very close agreement with the theoretical figures, owing to the readiness with which the salt dissociates, it nevertheless proves conclusively that the salt has the formula indicated above.

Salts of 2:6-Diphenylpyrazine.—The monohydrochloride of this base is described in the preceding paper (p. 2501). It is a practically colourless, crystalline solid. The *monohydrobromide*, however, is pale yellow, whilst the *monosulphate* is quite colourless. The *dihydrochloride* and *disulphate* were obtained in the form of solutions, both of which were yellow, but no positive indication of the formation of a dihydrobromide could be obtained.

2:6-Diphenylpyrazine monohydrobromide, $\text{C}_{16}\text{H}_{12}\text{N}_2(\text{C}_6\text{H}_5)_2 \cdot \text{HBr}$, separated in pale yellow needles on passing hydrogen bromide into a solution of the respective base in a mixture of ethyl acetate and alcohol. Like the previously described salts, it readily dissociated:

0.1108 gave 0.0840 AgBr . $\text{HBr} = 25.7$.

$\text{C}_{16}\text{H}_{12}\text{N}_2 \cdot \text{HBr}$ requires $\text{HBr} = 25.9$ per cent.

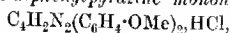
2:6-Diphenylpyrazine monosulphate, $\text{C}_{16}\text{H}_{12}\text{N}_2(\text{C}_6\text{H}_5)_2 \cdot \text{H}_2\text{SO}_4$, crystallised in quite colourless needles on adding concentrated sulphuric acid to a solution of 2:6-diphenylpyrazine in glacial acetic acid:

0.1316 gave 0.0934 BaSO_4 . $\text{H}_2\text{SO}_4 = 29.8$.

$\text{C}_{16}\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{H}_2\text{SO}_4 = 29.7$ per cent.

Salts of pp'-Dimethoxy-2:5-diphenylpyrazine.—The *monohydrochloride*, *monohydrobromide*, and *monosulphate* of pp'-dimethoxy-2:5-diphenylpyrazine crystallised readily, and the *disulphate* was also obtained in crystals, although it was very unstable. A solution of the *dihydrobromide* was obtained as a deep violet-coloured liquid by saturating a solution of pp'-dimethoxy-2:5-diphenylpyrazine in glacial acetic acid with hydrogen bromide; and this salt also appeared to be formed on passing dry hydrogen bromide over the solid base. No positive evidence of the formation of a dihydrochloride could be obtained.

pp'-Dimethoxy-2:5-diphenylpyrazine monohydrochloride,



was formed by saturating a warm solution of the pyrazine derivative in glacial acetic acid with hydrogen chloride. On cooling, the salt separated in bright yellow needles:

0.3191 gave 0.1374 AgCl . $\text{HCl} = 10.9$.

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{HCl}$ requires $\text{HCl} = 11.1$ per cent.

This salt dissociated much more readily than the corresponding

derivative of the 2:6-substituted base, and, when dissolved in chloroform, exhibits an intense green fluorescence.

pp'-Dimethoxy-2:5-diphenylpyrazine monohydrobromide,
 $C_4H_3N_2(C_6H_4 \cdot OMe)_2 \cdot HBr$,

was prepared in a manner similar to the salt last described. It formed orange-coloured needles:

0.2781 gave 0.1373 AgBr. $HBr = 21.3$.

$C_{13}H_{16}O_2N_2 \cdot HBr$ requires $HBr = 21.7$ per cent.

pp'-Dimethoxy-2:5-diphenylpyrazine monohydrobromide, like the corresponding hydrochloride, is fluorescent in chloroform solution.

pp'-Dimethoxy-2:5-diphenylpyrazine monosulphate,
 $C_4H_3N_2(C_6H_4 \cdot OMe)_2 \cdot H_2SO_4$,

separated in yellow needles on adding sulphuric acid to a warm solution of the respective base in glacial acetic acid, and cooling the mixture. It dissociates readily, and, like the last-mentioned two salts, is fluorescent in chloroform solution:

0.2700 gave 0.1581 $BaSO_4$. $H_2SO_4 = 24.6$.

$C_{13}H_{16}O_2N_2 \cdot H_2SO_4$ requires $H_2SO_4 = 25.1$ per cent.

When to a solution of *pp'*-dimethoxy-2:5-diphenylpyrazine in chloroform, concentrated sulphuric acid was added, a yellow solution of the monosulphate was first formed, which exhibited a brilliant green fluorescence, but on introducing an excess of the acid the base was dissolved by the latter, yielding an intensely violet-coloured liquid below the chloroform. Sufficient ethyl acetate was then added to render the mixture homogeneous, and the liquid kept a few hours, when *pp'*-dimethoxy-2:5-diphenylpyrazine disulphate, $C_4H_3N_2(C_6H_4 \cdot OMe)_2 \cdot 2H_2SO_4$, separated in small prisms, resembling in colour crystals of potassium permanganate. This disulphate is very unstable; it dissociates in ordinary air, yielding the yellow monosulphate, and, if the air be unusually damp, complete dissociation ensues. The dissociated mixture may, however, be successively reconverted into the yellow monosulphate and the deep violet-coloured disulphate by decantation:

0.1224 gave 0.1200 $BaSO_4$. $H_2SO_4 = 41.1$.

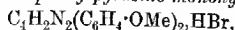
$C_{13}H_{16}O_2N_2 \cdot 2H_2SO_4$ requires $H_2SO_4 = 40.2$ per cent.

This disulphate dissociated so readily that it could not be washed with any solvent, and it is owing to this fact that the analysis indicated a somewhat high percentage of sulphuric acid.

Salts of pp'-Dimethoxy-2:6-diphenylpyrazine.—This base readily yielded a crystalline monohydrochloride, monohydrobromide, and monosulphate, the first of which has been described in the preceding

paper (p. 2546). No indication of the formation of a dihydrochloride could be obtained, but the *dihydrobromide* was obtained as a very deep violet-coloured solid by passing dry hydrogen bromide over the solid base. A deep violet-coloured solution of the *dihydrobromide* in concentrated sulphuric acid was formed, but this salt could not be crystallised.

pp'-Dimethoxy-2: 6-diphenylpyrazine monohydrobromide,



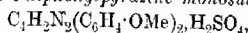
crystallised in deep yellow needles on the addition of a little concentrated hydrobromic acid to a solution of the base in a mixture of ethyl acetate and alcohol:

0.1655 gave 0.0832 AgBr. $\text{HBr}=21.3$.

$\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HBr}$ requires $\text{HBr}=21.7$ per cent.

This salt is not fluorescent, thus differing from its 2: 5-substituted congener.

pp'-Dimethoxy-2: 6-diphenylpyrazine monosulphate,



was obtained on adding concentrated sulphuric acid to a solution of the respective base in ethyl acetate. It was not fluorescent, and formed pale yellow needles, which dissociated fairly readily:

0.1635 gave 0.1549 BaSO_4 . $\text{H}_2\text{SO}_4=24.7$.

$\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{H}_2\text{SO}_4$ requires $\text{H}_2\text{SO}_4=25.1$ per cent.

Salts of mm'pp'-Tetramethoxy-2: 5-diphenylpyrazine.—The amount of this base available was very small, and therefore only its behaviour towards sulphuric acid was investigated. It was markedly more basic than the previously mentioned bases. When treated with a small amount of sulphuric acid in glacial acetic acid solution, it yielded *mm'pp'-tetramethoxy-2: 5-diphenylpyrazine monosulphate*, $\text{C}_6\text{H}_5(\text{OMe})_2\cdot\text{C}_4\text{H}_2\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OMe})_2\cdot\text{H}_2\text{SO}_4$, which formed orange-red needles. If, however, the solution contained an excess of sulphuric acid, the orange-coloured crystals of the monosulphate soon gave place to small, jet-black prisms of the corresponding *disulphate*, $\text{C}_6\text{H}_5(\text{OMe})_2\cdot\text{C}_4\text{H}_2\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OMe})_2\cdot 2\text{H}_2\text{SO}_4$. These crystals possessed a brilliant metallic lustre, and were permanent in the air, although they were dissociated fairly readily by alcohol. A dilute solution of *mm'pp'-tetramethoxy-2: 5-diphenylpyrazine disulphate* in concentrated sulphuric acid had an intensely blue colour. The amount of these salts was not sufficient for analysis.

Salts of mm'pp'-Tetramethoxy-2: 6-diphenylpyrazine.—This base readily yielded a crystalline monohydrochloride, monohydrobromide, and monosulphate, but no di-acid salt of it could be crystallised. No evidence of the existence of a dihydrochloride could be obtained, at a compound of a bluish-black colour with a bronze lustre, which

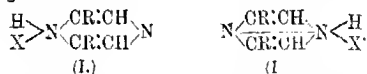
was doubtless the *dihydrobromide*, was obtained by passing dry hydrogen bromide over the crystalline base. A deep blue-coloured solution of the *disulphate* in concentrated sulphuric acid was also obtained.

mm'pp'-Tetramethoxy-2:6-diphenylpyrazine monohydrochloride, has been described in the preceding paper (p. 2511). It is deep yellow, and does not dissociate so readily as the previously described hydrochlorides.

mm'pp'-Tetramethoxy-2:6-diphenylpyrazine monohydrobromide, $C_6H_3(OMe)_2 \cdot C_4H_2N_2 \cdot C_6H_3(OMe)_2 \cdot HBr$, was obtained in orange coloured needles on passing hydrogen bromide into a solution of the respective base in warm ethyl acetate. The amount of product available was small, and it was not analysed.

mm'pp'-Tetramethoxy-2:6-diphenylpyrazine monosulphate, $C_6H_3(OMe)_2 \cdot C_4H_2N_2 \cdot C_6H_3(OMe)_2 \cdot H_2SO_4$, was prepared by adding concentrated sulphuric acid to a solution of the respective base in ethyl acetate. It formed yellow needles, which were stable in the air, but were dissociated by alcohol or water.

Two series of isomeric mono-acid salts of the 2:6-substituted pyrazines are possible, which would be represented respectively by the following formulæ:



Throughout the course of this work, however, no indication of the presence of isomerides was observed, and it is therefore probable that the acid attaches itself to one of the nitrogen atoms more readily than to the other. If this be the case, the mono-acidic salts of the 2:6-substituted pyrazines are probably represented by formula II. Furthermore, the fact that no di-acid salt of the last-mentioned bases could be crystallised may be due to these salts being difficult of formation, owing to steric hindrance, but it is quite likely that it is due only to their being more soluble than their 2:5-substituted isomerides.

In conclusion, the authors wish to acknowledge their indebtedness to Dr. J. T. Hewitt, who kindly placed at their disposal the spectroscope with which the curves given in this paper were obtained.

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CCLIX.—*The Absorption Spectra of Various Diketopyrroline Compounds.*

By JOHN EDWARD PURVIS.

A SERIES of coloured diketopyrrolines have been described by Ruhemann (Trans., 1909, **95**, 984, 1603; this vol., pp. 462, 1438), and it appeared to be of some interest to study these compounds in relation to their absorption and constitution; the aim of this communication is to show how far the absorption is connected with (1) the ketonic groups, (2) the replacement of the oxygen of the ketonic groups, and (3) the replacement of hydrogen of the aromatic side-chains by various groups.

N/1000-alcoholic solutions of the following substances were examined. The method of examination has been described before.

2:3-Diketo-4:5-diphenylpyrroline, $\begin{array}{c} \text{CO} \text{---} \text{CO} \\ | \qquad | \\ \text{CPh} : \text{CPh} \end{array} \text{>NH}$; dark red.

2:3-Diketo-4-phenyl-5-tolylpyrrolines (*o*-, *m*-, *p*-), $\begin{array}{c} \text{CO} \text{---} \text{CO} \\ | \qquad | \\ \text{CPh} : \text{C}(\text{C}_7\text{H}_7) \end{array} \text{>NH}$; dark red.

2:3-Diketo-4-phenyl-5-*p*-cumylpyrroline, $\begin{array}{c} \text{CO} \text{---} \text{CO} \\ | \qquad | \\ \text{CPh} : \text{C}(\text{C}_9\text{H}_{11}) \end{array} \text{>NH}$; dark red.

From the absorption curves (Fig. 1), it is evident that the absorptions are all of the same type. The differences correspond with differences in the shades of red of the different compounds. For example, the ortho-tolyl compound (I) is not quite so dark red as the meta- (III) and para- (V) compounds, and the curves show these differences, in that the rays are transmitted through greater thicknesses of the solution. It is noticeable, also, that the diphenyl compound (II) is a shade darker red than the ortho-tolyl compound, and not so deep red as the meta- and para-compounds. This is also clear from the curves, for the rays are transmitted through greater thicknesses than either the meta- or para-tolyl compounds. Or, to put it another way, the absorption band of the ortho-tolyl compound is not so strong as that of either the meta- or para-tolyl compound; and the absorption band of the diphenyl compound is a little stronger than that of the ortho-tolyl compound, but not so strong as the bands of the meta- or para-tolyl derivatives.

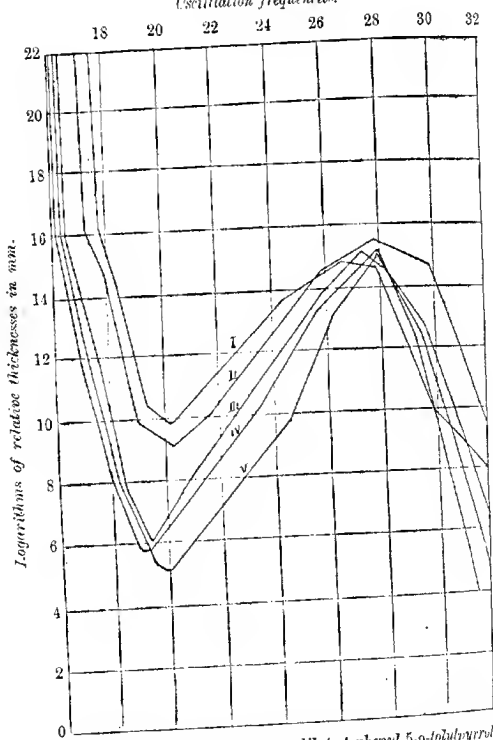
N/10,000-solutions of the substances were also examined, but no bands were observed in the ultra-violet regions. The positions

when general absorption begin, expressed in oscillation frequencies, are:

| | | |
|----------------------------------|--------------|------|
| Diketodiphenylpyrroline | 30 mm. thick | 3218 |
| " | 10 " " | 3697 |
| Diketo- <i>o</i> -tolylpyrroline | 30 " " | 3693 |
| " | 10 " " | 4100 |
| Diketo- <i>m</i> -tolylpyrroline | 30 " " | 3320 |
| " | 10 " " | 3951 |
| Diketo- <i>p</i> -tolylpyrroline | 33 " " | 3148 |
| " | 10 " " | 3965 |
| Diketo- <i>p</i> -cumylpyrroline | 30 " " | 3153 |
| " | 10 " " | 3593 |

FIG. 1.

Oscillation frequencies.



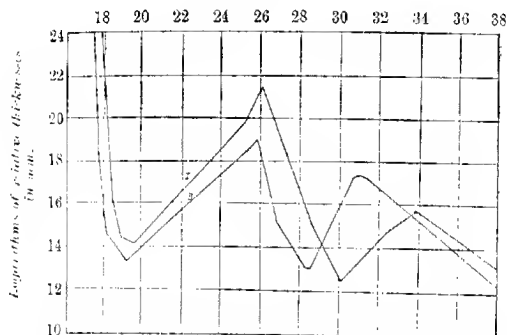
- I. N/1000-alcoholic solution of 2:3 diketo-4-phenyl-5-*o*-tolylpyrroline.
 II. N/1000-alcoholic " diketodiphenylpyrroline.
 III. N/1000-alcoholic " 2:3-diketo-4-phenyl-5-*m*-tolylpyrroline.
 IV. N/1000-alcoholic " 2:3-diketo-4-phenyl-5-*p*-cumylpyrroline.
 V. N/1000-alcoholic " 2:3-diketo-4-phenyl-5-*p*-tolylpyrroline.

Therefore the result of the substitution of hydrogen by an aliphatic group in an aromatic side-chain does not fundamentally alter either the colour or the absorption. The observed band corresponds in each case with the colour, and there is no band produced in the ultra-violet region.

When the two diketo-groups are still left intact, and the substitution in an aromatic side-chain is by the methoxy- or methylenedioxy-groups, the dark red colour remains unchanged, but another

FIG. 2.

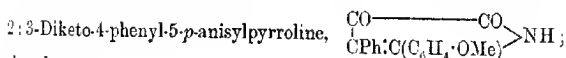
Oscillation frequencies.



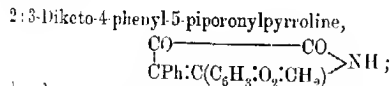
I. N/10,000-alcoholic solution of 2:3-diketo-4-phenyl-5-*p*-anisylpyrroline.

II. N/10,000-alcoholic „ 2:3-diketo-4-phenyl-5-piperonylpyrroline.

band in the ultra-violet region is produced. The formulæ of these two derived substances are:



dark red.



dark red.

N/10,000-solutions were examined, and from the curves (Fig. 2) it will be seen that each substance has two bands. The less refrangible band of each corresponds with the bands of the previous substances. On the other hand, the more refrangible bands have no corresponding bands in the original diphenyl compounds, and they also differ from each other both in position and persistency. In other words, neither the original colour nor the corresponding absorption is fundamentally altered by the introduction of a

methoxy- or a methylenedioxy-group in an aromatic side-chain, but another band is produced in the ultra-violet region corresponding with the new type of side-chain.

Further, the phenylhydrazones of the diphenyl compound and of the *p*-tolyl compound were examined in *N*/10,000-solutions. The constitutional formulae of these substances are:

Diketodiphenylpyrrolinephenylhydrazone,
$$\begin{array}{c} \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CO} \\ | \\ \text{CPh} \end{array} \text{---} \text{CPh} > \text{NH}.$$
 carmino red.

Diphenylpyrrolinophenazine,
$$\begin{array}{c} \text{CPh} \text{---} \text{C} \cdot \text{N} \\ | \quad | \\ \text{CPh} \cdot \text{NH} \cdot \text{C} \cdot \text{N} \end{array} > \text{C}_6\text{H}_4; \text{ lemon yellow.}$$

Diketophenyl-*p*-tolylpyrrolinephenylhydrazone,

$$\begin{array}{c} \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CO} \\ | \\ \text{CPh} \end{array} \text{---} \text{C}(\text{C}_6\text{H}_4) > \text{NH};$$
 carmine-red.

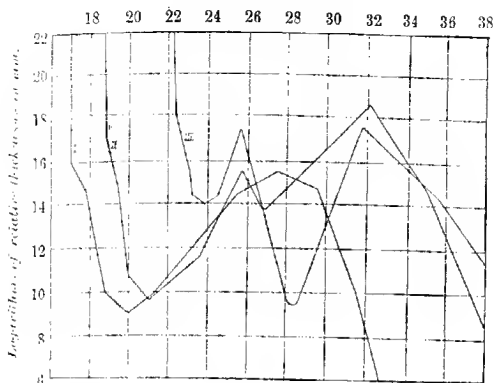
Phenyl-*p*-tolylpyrrolinophenazine,
$$\begin{array}{c} \text{CPh} \text{---} \text{C} \cdot \text{N} \\ | \quad | \\ \text{C}(\text{C}_6\text{H}_4) \cdot \text{NH} \cdot \text{C} \cdot \text{N} \end{array} > \text{C}_6\text{H}_4; \text{ lemon yellow.}$$

Considering the carmine-red phenylhydrazones, it will be seen from the curves (Fig. 3 and 4) that they show two bands. The less refrangible band corresponds with the single band of the original unsubstituted diketopyrrolines slightly shifted towards the more refrangible side; and the smaller, more refrangible one results from the introduction of the hydrazine radicle in place of oxygen of one of the ketonic groups. Considering the yellow-coloured phenazine compounds, the curves also show two bands, a smaller, less refrangible one, and a stronger one in the more refrangible side. That is to say, the successive elimination of the oxygen of both the ketonic groups produces a change in colour from dark red, through carmine-red to yellow; a decrease in the intensity of the band of the original diketonic substances; and the production of another band on the more refrangible side, the intensity of which increases by the successive elimination of the ketonic groups. It is important to notice that the increased weight of the molecule does not shift the band or the general absorption towards the red end, as is usually the case. On the contrary, the shift is towards the more refrangible end of the spectrum.

General Results and Discussion.

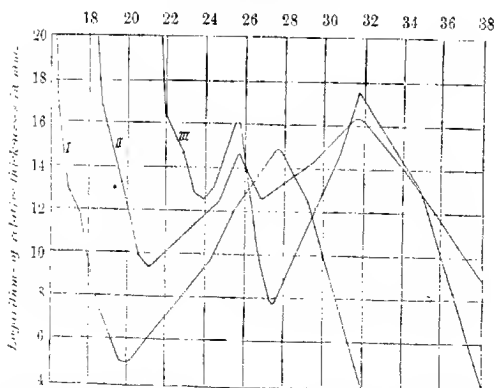
To sum up these observations, it is clear (1) that the diketonic structure means the production of a dark red colour, and a corresponding well-marked absorption band, the position of which differs slightly, corresponding with differences in the dark red shade; (2) the introduction of a methyl or

FIG. 3.

Oscillation frequencies.

- I. N/1000-alcoholic solution of diketodiphenylpyrroline.
 II. N/10,000-alcoholic " diketodiphenylpyrrolinophenylthiohydrazone.
 III. N/10,000-alcoholic " diphenylpyrrolinophenazine.

FIG. 4.

Oscillation frequencies.

- I. N/1000-alcoholic solution of 2:3-diketo-4-phenyl-5-p-tolylpyrroline.
 II. N/10,000-alcoholic " " phenylthiohydrazone.
 III. N/10,000-alcoholic " phenyl-p-tolylpyrrolinophenazine.

a propyl group in an aromatic side-chain produces no fundamental change either in the colour or in the absorption band; (3) if either a methoxy- or a methylenedioxy-group is introduced in an aromatic side-chain, the deep red colour and corresponding band are still retained, but another more refrangible band is produced characteristic of the type of the introduced radicle; (4) when one of the oxygen atoms of the diketonic groups is replaced by the $\text{:N}\cdot\text{NHPh}$ group, the colour is changed from dark red to carmine-red; the corresponding less refrangible absorption band is reduced in intensity and its position is shifted towards the more refrangible side; and another weaker band is produced beyond this on the more refrangible side; (5) the replacement of both oxygen atoms of the diketonic groups, and the production of the phenazine ring $\text{:N} \rightarrow \text{C}_6\text{H}_4$, changes the colour from carmine-red to lemon-yellow, and the corresponding band is also shifted towards the more refrangible end. This band is also less intense, and the second more refrangible band becomes much stronger; and (6) corresponding with these changes in colour and selective absorption, the positions of general absorption are shifted towards the more refrangible region of the spectrum.

The observations, then, indicate that the absorption is intimately connected with the presence of a diketonic grouping. Baly and Stewart (*Trans.*, 1906, **89**, 502) have suggested that the residual affinities of the dicarbonyl compounds studied by them are oscillating between two extreme phases. But in these compounds it may be equally valid to say that the maximum valencies of the oxygen atoms come into action, resulting in the production of a closed ring produced by the two oxygen atoms, and the consequent production of absorption. On this suggestion the ring is destroyed by the elimination of the oxygen in the hydrazone linking; the intensity of the original band is lessened, and another band is produced, accompanied by changes in the colour and absorption in the visible spectrum from the less to the more refrangible regions. The further production of the phenazine ring does not wholly destroy the original absorption; it simply decreases it, and another band is produced characteristic of the new type of ring.

From these considerations, it seems to be difficult to resist the conclusion that the original band, which corresponds with the deep red colour, is caused by the oscillation or vibration of the original diketopyrroline ring, and that it is modified by the elimination of the ketonic groups. In connexion herewith, it should be mentioned that the author found no bands in phenylhydrazine in solutions of $N/10$, $N/100$, $N/1000$, and $N/10,000$ -strengths

through varying thicknesses of 2 mm. to 30 mm. Also, Hartley and Dobbie (*Trans.*, 1898, **73**, 598) found no bands in alcoholic solutions of pyrrole, and this has been confirmed by the author (this vol., p. 1648).

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the spectroscope used in this research was obtained, and also Dr. Ruhemann for specimens of the pure substances.

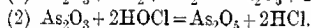
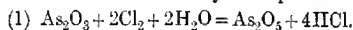
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CCLX.—*Researches on Bleaching Powder.*

By ROBERT LLEWELLYN TAYLOR.

For the purpose of this investigation, it was first of all necessary to devise a method for distinguishing between pure chlorine and hypochlorous acid, and, in a mixture of the two, finding their proportions.

The method used was to pass the gases through a known volume of *N*/10 sodium arsenite. The action of chlorine and of hypochlorous acid on sodium arsenite may be represented thus:



It is plain that, for the same amount of arsenite oxidised, twice as much hydrochloric acid (or chloride) is produced in the case of chlorine as in the case of hypochlorous acid. The arsenite (which must always be in excess, so that it is not completely oxidised) is then divided into two equal parts. In one-half, the amount of arsenite remaining unoxidised is determined by means of *N*/10 iodine solution, and from this the amount oxidised is ascertained. In the other half, the amount of chlorine is determined by means of *N*/10 silver nitrate. In the latter determination the use of an indicator was very soon discarded, although, if a considerable proportion of the arsenite has been oxidised, the arsenate produced acts fairly well as an indicator, and may be used instead of adding a chromate to the solution. Much more trustworthy results, however, are obtained by acidifying the solution with nitric acid, adding a little of the silver solution, boiling for a minute or two, and then filtering a portion of the liquid. A little more of the silver solution is added, drop by drop, to the filtered portion, which

is then returned to the bulk, and this boiled and filtered again. This is continued until the filtered portion gives no further precipitate with the silver solution. As described, the process seems tedious, but in practice it works very well, and the determination of the chlorine can be made fairly rapidly. In this process, as the solutions used are all decinormal, and therefore equal to each other, when the oxidising agent is pure chlorine, the amount of silver nitrate used (=amount of chloride present) is the same as the amount of arsenite oxidised. When hypochlorous acid is the oxidising agent, the chloride produced is only half the amount of arsenite oxidised.

The Action of Carbon Dioxide on Bleaching Powder.

It is very frequently stated, and probably usually considered, that carbon dioxide simply liberates hypochlorous acid from bleaching powder. A considerable number of observers, however, have pointed out that chlorine is produced when pure carbon dioxide acts on bleaching powder.

Thus, Richards and Juncker (*Dingl. Polyt. J.*, 1874, 211, 31) state that dry bleaching powder is almost undecomposed by carbon dioxide. If about 10 per cent. of water is present, both chlorine and hypochlorous acid are produced.

Wolters (*J. pr. Chem.*, 1874, [ii], 10, 128) refers to the liberation of chlorine by the action of carbon dioxide on bleaching powder, and Lunge and Schäppi (*Dingl. Polyt. J.*, 1889, 273, 63) state that carbon dioxide expels nearly the whole of the chlorine from bleaching powder.

Dreyfus (*Bull. Soc. chim.*, 1884, [ii], 41, 600) found that carbon dioxide has no action on calcium chloride, but, in the presence of chlorine monoxide, either dry or in aqueous solution, it liberates chlorine.

More recently this question, with others relating to bleaching powder, has been investigated by von Tiesenholt (*J. pr. Chem.*, 1901, [ii], 63, 30; 1902, [ii], 512; 1906, [ii], 73, 301). Some of his conclusions will be referred to later.

In my first experiments, carbon dioxide, in its ordinary moist condition, after being well washed with water, was passed through a U-tube containing bleaching powder and a sufficient amount of glass wool to give a free passage for the gas. Carbon dioxide, as ordinarily prepared by the action of hydrochloric acid on marble, invariably carries with it a little hydrochloric acid, and, in some of the experiments, this was removed by passing the gas through glass wool wetted with a solution of silver nitrate, which acts quite effectually. When, however, the gas is well washed with water, the

amount of hydrochloric acid accompanying it is not sufficient seriously to affect the results. After passing through the bleaching powder, the gas was passed through a Bunsen U-tube containing N/10-sodium arsenite.

A considerable number of experiments were made, and the following is an example of the results invariably obtained. Twenty c.c. of the N/10-arsenite were used:

I.

| | |
|--|-----------|
| Amount of arsenite oxidised | 8.35 c.c. |
| Amount of N/10-silver nitrate used | 8.4 c.c. |

It is plain from this that the sole product of the action of carbon dioxide on bleaching powder is chlorine. The escaping gas has a strong odour of chlorine, and none at all of hypochlorous acid. The action proceeds very rapidly if the carbon dioxide is quite moist.

In some further experiments, the carbon dioxide was dried by passing it over calcium chloride. The effect of drying the gas is that the action becomes much slower, and, as the moisture usually present in the bleaching powder is gradually carried away by the dry carbon dioxide, it soon becomes extremely slow. When this point has been reached, the instantaneous acceleration of the action when the drying tube is removed is very striking. The following three experiments show that the product is the same with the dry with the moist gas, namely, nothing but chlorine:

II.

| | Arsenite oxidised. | Chloride produced. |
|----|--------------------|--------------------|
| 1. | 3.4 | 3.5 |
| 2. | 1.9 | 1.95 |
| 3. | 6.55 | 6.65 |

The slight excess of silver nitrate used may have been due to a little hydrochloric acid carried over, although the actual amounts are not beyond the limits of accuracy of the method.

When carbon dioxide is passed through a solution of bleaching powder in water, the action is very rapid, but the result is exactly the same, as the following experiments show:

III.

| | Arsenite oxidised. | Chloride produced. |
|----|--------------------|--------------------|
| 1. | 5.6 | 5.58 |
| 2. | 3.1 | 3.1 |

The escaping gas again had a strong odour of chlorine, and none at all of hypochlorous acid.

Action of Carbon Dioxide on a Mixture of Sodium Chloride and Hypochlorite, and on a Mixture of Bromide and Hypobromite.

The mixture of sodium chloride and hypochlorite was prepared by passing chlorine into a moderately concentrated cold solution of sodium hydroxide. The following experiments show that the action is exactly the same as with a solution of bleaching powder:

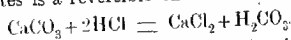
IV.

| | Arsenite oxidised. | Chloride produced. |
|----|--------------------|--------------------|
| 1. | 4.1 | 4.12 |
| 2. | 6.1 | 6.13 |

When carbon dioxide is passed through a solution containing a mixture of a bromide and a hypobromite there is, as one would naturally expect, an immediate and copious liberation of bromine.

It is well known that carbon dioxide acts in a similar way on a mixture of iodide and hypoiodite.

It appears, from the foregoing experiments, that the action of carbonic acid on bleaching powder and similar substances is exactly like that of any other acid. There has been much discussion as to the actual constitution of dry bleaching powder, but, whatever that constitution may be, it may be taken that, in solution or in presence of water, it is, to all intents and purposes, a mixture of chloride and hypochlorite. The usual explanation of the action of, say, sulphuric acid (when used in considerable quantity) on bleaching powder is that the chloride and hypochlorite are both decomposed, with the simultaneous production of hydrochloric and hypochlorous acids, and that these decompose each other, with the liberation of chlorine. The question is whether or not we must seek for some other explanation of the action of carbonic acid. There would seem to be no doubt that the action of carbonic acid is exactly like that of other acids. Of course, this involves the conclusion that calcium chloride (or sodium chloride, for example) is decomposed, when in solution, by carbonic acid, with the liberation of hydrochloric acid, and that, therefore, the action of hydrochloric acid on carbonates is a reversible one:



I have tried to obtain some experimental evidence that this is the case, and not altogether without success.

Many years ago Müller (*Journ. Chem. Soc.*, 1870, 23, 36) stated that a solution of lead chloride is decomposed when carbon dioxide is passed through it, with liberation of hydrochloric acid and precipitation of a chlorocarbonate, and that some of the liberated acid could actually be distilled off. He also stated that carbon dioxide

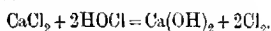
under considerable pressure, would decompose sodium and calcium chlorides, when in solution in water, with liberation of hydrochloric acid. He used ultramarine as an indicator, and stated that, whilst carbon dioxide alone does not decompose ultramarine suspended in water, even under considerable pressure, if the water contains common salt dissolved in it the colour of the ultramarine is destroyed.

I am unable to confirm the latter observation. Carbon dioxide, when bubbled through water in which a little ultramarine is suspended, has no effect on it, whether the water contains salt or not. Under a pressure of a few atmospheres, however, ultramarine is decomposed and decolorised by carbonic acid alone, and I have been unable to observe any difference in the action when the water contained salt as well. The experiments I made were performed in an ordinary sparklet apparatus, in which the pressure attains five or six atmospheres. If distilled water with a little ultramarine suspended in it is placed in such an apparatus, and then the liquid charged with carbon dioxide in the usual way, there is no immediate effect, but, in the course of a day or two, the colour of the ultramarine gradually disappears. As stated above, the presence of salt (or of calcium chloride) in the water makes no apparent difference in the result.

Methyl-orange is, however, a much more delicate indicator for acids than ultramarine. It is usually assumed that the former is not affected by carbonic acid, but this is not quite correct. If well washed carbon dioxide is bubbled through distilled water containing a little methyl-orange, there is a distinct alteration of the colour, though it does not turn pink. If, however, the water contains also a little pure salt, or calcium chloride, or potassium chloride, the colour becomes distinctly pink when the carbon dioxide is bubbled through. The change of colour is most striking in the case of the common salt, but it is quite evident with the other chlorides. This may be taken as evidence that carbonic acid liberates a sensible amount of hydrochloric acid in solutions of chlorides, that is to say, the action of hydrochloric acid on carbonates is a reversible one. Of course, the amount of hydrochloric acid thus liberated must be extremely small, but it will be quite sufficient to explain the action of carbonic acid on bleaching powder and similar substances. The small amount of hydrochloric acid liberated will be at once decomposed by the hypochlorous acid liberated simultaneously from the hypochlorite; this will enable the action of the carbonic acid to proceed as before, and so there will be a continuous evolution of chlorine, and, if this is carried away as fast as it is formed, the bleaching powder will be almost completely decomposed.

It may here be noted that if carbon dioxide is bubbled through water containing potassium bromide or ammonium chloride and coloured with methyl-orange, the change of colour is not so striking as in the case of the three chlorides mentioned above. Pure water coloured with methyl-orange becomes quite pink when charged with carbon dioxide in a sparklet apparatus.

Von Tiesenholt (*loc. cit.*) explains the production of chlorine when carbon dioxide acts on bleaching powder by supposing that hypochlorous acid is first formed by the action of the carbon dioxide on the hypochlorite present, and that this acts on the calcium chloride, liberating chlorine:



He finds, in confirmation of this view, that chlorine is liberated when a solution of hypochlorous acid is added to calcium chloride or to common salt. The experiments here described, however, show that nothing but chlorine is produced by the action of carbonic acid on bleaching powder, so that all the hypochlorous acid which is liberated must be decomposed. Apparently, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a sufficient amount of a chloride, so that it would be impossible to expel any hypochlorous acid from a solution which contains chlorides. As will be seen later, however, mixtures of chlorine and hypochlorous acid containing a considerable proportion of the latter can be expelled from solutions of bleaching powder. Consequently, whilst it is possible that the action of hypochlorous acid on chlorides may account for some of the chlorine which is produced in the case of concentrated solutions or the merely moist bleaching powder for example, von Tiesenholt's explanation would not appear to be preferable to the one offered above.

The Action of Air on Bleaching Powder.

Although this was not the order in which the experiments were actually tried, it will be best to describe first the effect of air from which all the carbon dioxide has been removed. This was done by passing the air through washing cylinders containing coke wet with a concentrated solution of sodium hydroxide. It was then bubbled through a milky solution of bleaching powder (about 5 to 10 per cent.), and afterwards through the solution of sodium arsenite.

In all the experiments with air, it was passed through at a rate of about 10 to 15 litres per hour.

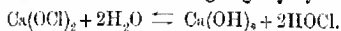
Air free from carbon dioxide is practically inert so far as bleaching powder is concerned, and naturally all that it can do is to sweep out any chlorine or hypochlorous acid which may happen to be present. Consequently, the action is very slow, and the experi-

ments had to be carried on for a long time (from seventy-two to ninety-six hours) in order to obtain sufficient oxidising action in the solution of arsenite to be able to judge what was being carried over. The following results were obtained in three separate experiments:

V.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 1.08 | 0.57 | 90 | 10 |
| 2. | 1.0 | 0.45 | 100 | 0 |
| 3. | 0.8 | 0.38 | 100 | 0 |

The amount of oxidation in these experiments was very little, but they appear to show that a small amount of free hypochlorous acid exists in a solution of bleaching powder, which is simply swept out by the passage of air free from carbon dioxide through it. Probably the free hypochlorous acid is due to the calcium hypochlorite in a dilute solution being slightly hydrolysed, thus:



This possibly accounts for the fact that solutions of bleaching powder have an odour of hypochlorous acid.

One similar experiment to the above was made in which the solution of bleaching powder was kept at a temperature of about 40° the whole of the time. In this experiment, also, practically nothing but hypochlorous acid was swept out, the only difference being that, as one would expect, the time required was rather less.

Action of Ordinary Air on Bleaching Powder.

A considerable number of experiments were made with ordinary air, passing it through a tube containing dry bleaching powder, and then through the solution of arsenite. At first the action is rather slow, but, as the bleaching powder gradually becomes wet, the action proceeds more and more rapidly. In some of the experiments the moisture of the air was purposely increased by passing it through a tube containing wet glass wool. In each of the two following series of experiments the same tube of bleaching powder was used throughout. The time occupied by each experiment varied from about twenty-four hours at the beginning to six hours when the bleaching powder had become wet:

VI.

Series 1.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 4.45 | 4.0 | 11 | 89 |
| 2. | 2.9 | 2.56 | 13 | 87 |
| 3. | 2.55 | 2.3 | 10 | 90 |
| 4. | 7.0 | 6.95 | 0 | 100 |
| 5. | 7.9 | 7.95 | 0 | 100 |

Series 2.

| | | | | |
|----|------|------|----|-----|
| 1. | 2.1 | 1.83 | 15 | 85 |
| 2. | 3.35 | 3.1 | 8 | 92 |
| 3. | 6.0 | 6.05 | 0 | 100 |

The above experiments are selected from a considerable number, and they all tend to show that, at the outset, ordinary air sweeps out from bleaching powder a mixture containing from 80 to 90 per cent. of chlorine, and from 10 to 20 per cent. of hypochlorous acid, but that, as the action proceeds, the amount of hypochlorous acid gradually diminishes, and at last nothing but chlorine appears. The gradation of the experiments is not the same in the two series, but that is partly due to the fact that some intermediate experiments in both series were spoiled by going on too long.

When ordinary air is passed through a solution of bleaching powder (not filtered, and containing about 5 to 10 per cent. of the powder), the proportion of hypochlorous acid swept out is considerably greater, as indeed one would expect if we accept the suggestion that the hypochlorous acid is due to hydrolysis of the calcium hypochlorite. As in the case of the dry powder, however, the amount of hypochlorous acid gradually diminishes as the experiment proceeds, although it does not disappear altogether. The following experiments were made with the same solution of bleaching powder, in the order in which they are given. In experiment No. 4, the proportion of hypochlorous acid appears to have risen slightly, but the method of determining it is not accurate enough to enable one to say that the amounts in experiments 3 and 4 were not substantially the same. The action was very slow in the first experiment, but much more rapid afterwards:

VII.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 4.48 | 2.94 | 52 | 48 |
| 2. | 9.15 | 7.27 | 25 | 75 |
| 3. | 3.18 | 2.88 | 10 | 90 |
| 4. | 3.34 | 2.87 | 16 | 84 |

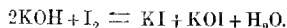
It must be pointed out that the above numbers, showing the actual amounts of hypochlorous acid and chlorine swept out of the liquid by the air, do not necessarily represent the actual proportions present at any moment in the liquid itself. There is no doubt that chlorine, being less soluble in water than hypochlorous acid, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the above numbers indicate.

These results, showing the action of ordinary air on bleaching powder, are very remarkable. The difference between the action of ordinary air and air from which the carbon dioxide has been removed is, at first sight, almost incredible. Whereas the latter simply sweeps out from a solution of bleaching powder (although very slowly) practically pure hypochlorous acid, the presence of the really very small amount of carbon dioxide which usually exists in ordinary air causes the action to proceed much more rapidly although not with anything like the rapidity with which pure carbon dioxide acts), and, after a time, has almost the same effect, as far as the product is concerned, as passing pure carbon dioxide through it.

I have already expressed the opinion that the action of pure carbon dioxide on bleaching powder is the same as that of the acids—it is a mass action, and the carbonic acid decomposes all the chloride and the hypochlorite. Whilst one may accept no explanation in the case of pure carbon dioxide used in comparatively large quantities, and always locally in large excess, it is possible to believe that the small amount of carbon dioxide present in ordinary air can act in the same way. We must therefore look for some other explanation.

The Action of Chlorine on Alkalis a Reversible Action.

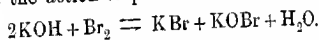
In former papers (*Mem. Manchester Phil. Soc.*, 1897, **41**, No. III; *Trans.*, 1900, **77**, 725) I have pointed out that the action of iodine on alkalis is a reversible one. If an alkali is added to a solution of iodine in water or in potassium iodide until the colour just disappears, the addition of potassium iodide to the solution causes the liberation of some of the iodine:



The addition of the extra amount of potassium iodide causes the action to proceed from right to left in the above expression. I.e. and this, too, follows from the fact that the action is reversible, the amount of alkali needed to complete the reaction from left to right and to remove the colour of the iodine is considerably more

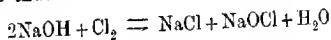
than is required by the equation, so that the almost colourless solution of iodide and hypiodite always contains some free alkali.

When these experiments were made, similar ones were also performed with bromine and alkalis, but analogous results were not obtained. The reason of this must have been that too strong a solution of bromine was used, because I find that the reversibility of the action of bromine on alkalis is quite as striking as that of iodine if a very dilute solution of bromine is employed. The action is not nearly so easy to see with ordinary bromine water, but if this is diluted with ten to twenty times its bulk of water, and then sodium or potassium hydroxide added drop by drop until the colour of the bromine has disappeared, the addition of a little concentrated solution of potassium bromide causes a manifest liberation of bromine. The liberation of bromine is seen still more plainly if, instead of the solution of potassium bromide, a considerable amount of the powdered salt is added. The addition of the extra potassium bromide causes the action to proceed from right to left:

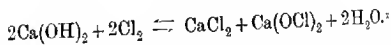


It is perfectly reasonable to suppose, then, that the action of chlorine on alkalis is also a reversible action. This has already been suggested by von Tiesenholtz (*loc. cit.*), who describes a number of experiments which point to this conclusion. I have been able to demonstrate, by experiments which are described later, that this conclusion is correct, and it will be seen that it supplies a perfectly satisfactory explanation of the action of ordinary air on bleaching powder, and that it also explains some well-known facts with regard to some bleaching solutions which have been hitherto apparently inexplicable.

If we represent the action of chlorine on sodium hydroxide and on slaked lime thus:



and



it is plain that the chlorides produced by the action are continually tending to reverse the reaction, so that, to carry it to a finish from left to right, there must always be a considerable amount of free sodium hydroxide or lime present. It is a well-known fact that bleaching powder always contains a considerable amount of free lime, and that it is impossible to prepare it otherwise. If this free lime, or a portion of it, is removed, then the reaction will proceed

* It is not suggested that this equation represents what actually occurs in the manufacture of bleaching powder, but simply the condition of equilibrium in which it exists when wet or in solution.

in the opposite direction to a greater or less extent, and chlorine will be liberated.

A number of experiments were made to test this point. A filtered solution of bleaching powder was employed, having a specific gravity of 1.03 to 1.06 in different experiments. In order to remove some of the free lime, the solution was exposed to air for some hours in a shallow dish, with occasional shaking. The amount of free lime present in such a solution is considerable, and the latter becomes very milky on exposure to air. The liquid was filtered from the precipitated calcium carbonate, and air free from carbon dioxide was passed through it and into the arsenite solution in the usual way. The following are some of the results obtained:

VIII.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 4.9 | 3.16 | 26 | 74 |
| 2. | 3.8 | 3.0 | 27 | 73 |
| 3. | 2.8 | 1.8 | 44 | 56 |
| 4. | 5.92 | 5.15 | 15 | 85 |
| 5. | 4.35 | 4.04 | 8 | 92 |
| 6. | 2.27 | 1.52 | 50 | 50 |

Most of the separate experiments were made with different portions of the solution, which had been exposed to air for different lengths of time, so that the extent to which the free lime was removed varied. Doubtless this accounts for the irregularity in the results. In all the above experiments the action was much more rapid than was the case with the solution from which none of the free lime had been removed, the rapidity evidently depending on the extent to which this removal had been carried. It will be noted that besides the large quantities of free chlorine produced, in most of the experiments the amount of hypochlorous acid swept out from the liquid was very much greater than was the case with the solution from which no free lime had been removed. This is quite what one would expect to occur. The hypochlorous acid, as before stated, is probably due to hydrolysis of the calcium hypochlorite in the solution. This also is a reversible action, and as one of the products of the hydrolysis is free lime, the removal of the free lime naturally stimulates this action as well.

These experiments demonstrate quite sufficiently the reversibility of the reaction between chlorine and calcium hydroxide. As the free lime is more or less removed, the reaction proceeds in the opposite direction, and chlorine is liberated. In these experiments the free chlorine is swept out of the solution, but it is continually being reproduced, the steady removal of the chlorine allowing the

reverse action to take place continuously. If the free chlorine were removed from the solution in any other way, by bleaching, for example, it would in the same way be continually reproduced as long as any of the bleaching substance remained. It follows from this, of course, that the bleaching action of a solution of bleaching powder will be stimulated by the removal of free lime from the solution. This will be referred to again later.

The action of ordinary moist air on bleaching powder, both solid and in solution, described on p. 2548, is now perfectly intelligible. The carbon dioxide in the air combines with the free lime, and, as this gradually diminishes and finally practically disappears, the reverse action proceeds freely, and, of course, chlorine is produced.*

It is usually understood, and has been frequently stated, that a pure solution of hypochlorous acid bleaches more energetically and more rapidly than free chlorine. It may be doubted whether this is really the case. I have prepared practically pure solutions of hypochlorous acid, and compared its action with that of a solution of chlorine on various colouring matters, and I have failed to find any evidence of the greater activity of hypochlorous acid. Rather the contrary. With a solution of indigo-carmin, for example, the bleaching action of chlorine is much more rapid than that of hypochlorous acid—in the case of the latter the action is to be described as sluggish, rather than rapid. This is an important point, because I am strongly of opinion that in the use of solutions of bleaching powder and similar substances for bleaching purposes, most of the actions generally attributed to hypochlorous acid are really due to chlorine, and that, in practice, hypochlorous acid plays only a minor part in bleaching.

It is remarkable how the bleaching action of a solution of bleaching powder is stimulated by the mere removal of the free lime in it. If a strip of Turkey-red calico is placed in a clear solution of bleaching powder so that it is completely immersed in the liquid, and if the liquid is kept in a closed vessel so that air has no access to it, there is scarcely any bleaching action at all, even after several days. If, however, the solution is placed in a

* It may be asked if the removal of free lime by carbon dioxide is a satisfactory explanation of the fact that ordinary air expels chlorine from bleaching powder, so that there would be no need to assume, as is done in the first part of this paper, that carbonic acid decomposes chlorides with the liberation of hydrochloric acid. The author adheres to the latter explanation simply because the action of carbon dioxide is so much more rapid than that of air. A stream of carbon dioxide through a solution of bleaching powder liberates chlorine from ten to twenty times more rapidly than air at its quickest, and the action altogether suggests a rapid and complete decomposition, such as is effected by other acids, rather than the mere sweeping out of chlorine produced by the reversed action.

basin or a shallow dish, so that air has free access, and if a small portion of the red calico is left outside the liquid, so that it is reached by the solution and the air at the same time, the portion outside is bleached quite rapidly. Further, if the coloured calico is completely immersed in a little of the solution contained, say, in a deep test-tube, and the test-tube is breathed into about half a dozen times, shaking after each time, the calico is very soon bleached. Also, whilst, as stated above, a fresh solution of bleaching powder has very little, if any, bleaching action on a piece of red calico completely immersed in it, if the solution has been exposed to air in a shallow dish for a few hours, with occasional shaking, then a piece of red calico completely immersed in it is bleached rapidly.

A simple but very striking experiment which illustrates the same point is to immerse a strip of ordinary red litmus paper in a fresh solution of bleaching powder. The paper is turned blue, and in a short time it is bleached. If, however, immediately after it has been dipped in the solution, it is breathed upon, it is bleached almost instantly. A solution of bleaching powder which has been well exposed to air, as described above, bleaches litmus paper at once.

In all these cases the more rapid bleaching action is simply due to the removal of free lime, and I think it is plain, also, if reference is made to the experiments, series VIII, on p. 2551, that the principal bleaching agent is chlorine, and not hypochlorous acid. Certainly those experiments show that in some cases a considerable proportion of hypochlorous acid is swept out, but in all cases the rapidity of the bleaching action is roughly proportional to the extent to which the free lime is removed, and the more completely that is done the greater is the proportion of chlorine liberated.

It is a fact, well known in bleach-works, that an old vat is more active than a new one. The reason for this is obvious. Exposure to air, especially if the liquid is frequently stirred, gradually causes the removal of the free lime.

If the action of chlorine on lime is, as I think the above experiments sufficiently demonstrate, a reversible action, then the reverse action must be stimulated by the addition of calcium chloride to the solution. Experiments were made to see if this is the case. After experiment No. 2 (series VIII) on p. 2551 was finished, a considerable amount of crystallised calcium chloride was added to the same solution of bleaching powder and air free from carbon dioxide passed through it again. The action became considerably more rapid, and the effect of the calcium chloride is seen by a comparison

of the two experiments. No. 1 was before, No. 2 after, the addition of the calcium chloride.

IX.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 3.8 | 3.0 | 27 | 73 |
| 2. | 4.75 | 4.73 | 0 | 100 |

The solution used in experiment No. 6 (series VIII) was treated in the same way with the following result:

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 2.27 | 1.52 | 50 | 50 |
| 2. | 5.4 | 4.92 | 10 | 90 |

These experiments show plainly that, as anticipated, the reverse action is greatly increased by the addition of more calcium chloride.

Other chlorides, of course, ought to have a similar effect. The following experiments show the effect of adding common salt to the solution. As before, the greater part of the free lime in the solution was removed by exposing it to air. Experiments 1 and 2 were successive experiments before the addition of the salt, and No. 3 shows the effect of the salt. The salt was added in considerable quantity—almost sufficient to saturate the solution.

X.

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 1.75 | 1.4 | 25 | 75 |
| 2. | 5.25 | 4.1 | 23 | 72 |
| 3. | 6.53 | 6.55 | 0 | 100* |

The addition of the salt in the above experiment caused the action to proceed much more rapidly. Thus, whilst in experiment No. 2 it took twenty hours to oxidise 5.25 c.c. of the arsenite solution, in experiment No. 3, 6.53 c.c. were oxidised in four hours, the carbon dioxide-free air passing through at approximately the same rate in both experiments.

* The apparently complete disappearance of hypochlorous acid indicated in experiments 2 (IX) and 3 (X) is very remarkable, and seems difficult to explain. It is not claimed, however, that the method used for determining the relative amounts of chlorine and hypochlorous acid is perfectly accurate. It is doubtful whether it would be possible to determine very small proportions of hypochlorous acid by it. It must also be borne in mind (see p. 2549) that chlorine is more easily swept out from the solution than hypochlorous acid, so that it is possible that the latter does not altogether disappear. Possibly, also, von Tiesenholz's explanation (see p. 2546) may apply here, and the hypochlorous acid may be all decomposed by the large quantities of chlorides present in the solution.

Experiments were also made to see the effect of the addition of calcium chloride and salt to an ordinary solution of bleaching powder, without removing any of the free lime. The free lime in the solution, of course, tends to stop the reverse action, so that the effect of adding calcium chloride or salt to the solution is not nearly so great as when the free lime is first removed. The following is the result of the two experiments tried.

To No. 1 calcium chloride was added, and to No. 2 common salt both in large quantity. The action proceeded very slowly indeed in both experiments, but the results are sufficient to show that, even in ordinary bleaching powder solution, the addition of chlorides has a sensible effect in reversing the action:

| | Arsenite oxidised. | Chloride produced. | Hypochlorous acid, per cent. | Chlorine, per cent. |
|----|-----------------------|-----------------------|------------------------------------|------------------------|
| 1. | 2.24 | 2.22 | 0 | 100 |
| 2. | 2.68 | 2.4 | 10 | 90 |

It follows from the above experiments that the addition of calcium chloride or salt to a solution of bleaching powder must exercise a stimulating effect on the bleaching action of the solution. This is actually the case. If some of the free lime has been removed from the solution, the effect of the addition of considerable amounts of calcium chloride or salt on the bleaching action is very striking. With bleaching powder solution in its ordinary state, containing the usual amount of free lime, the effect on its bleaching action of adding calcium chloride or salt is, for the reason pointed out above, not nearly so great, although it is quite sufficiently marked.

I understand that it has been found, in actual bleaching, that the addition of either calcium chloride or salt stimulates the action, but I am not aware that any satisfactory explanation of this stimulating effect has hitherto been given. It may perhaps be worth the while of practical bleachers to note that the addition of calcium chloride or salt has a much greater effect when some of the free lime has been removed—by exposing the solution to air, for example.

Bleaching solutions made by the electrolysis of a solution of salt have latterly come into considerable use, and I understand that the fact has been frequently noted that a solution of sodium hypochlorite thus prepared is more active than a solution of sodium hypochlorite, containing the same proportion of available chlorine, prepared by the addition of sodium carbonate to a solution of bleaching powder and allowing the precipitated calcium carbonate to settle. The explanation of this is obvious when it is understood that, in preparing the electrolytic bleaching solution, only a small fraction of the salt in the solution is usually decomposed. The

solution thus differs from that made by the other method by containing a large amount of salt, and the effect of this is to increase the reverse action and so to liberate chlorine in the solution. Also in the electrolysis of the salt, chlorine and sodium hydroxide are produced in exactly equivalent proportions, so that there cannot be a sufficient amount of the latter to absorb the whole of the chlorine. Under these conditions, the reversing action of the excess of salt will naturally be very considerable. The greater bleaching activity of such a solution is therefore perfectly natural, and exactly what one would expect.

In addition to the experiments described in this paper, I have used my method for distinguishing between hypochlorous acid and free chlorine for investigating the action of various acids on bleaching powder and similar substances. This investigation is still proceeding.

Summary.

1. The action of carbon dioxide on bleaching powder and similar substances results in the liberation of chlorine only—not hypochlorous acid. The conclusion is drawn that the action is like that of any other acid, and that carbonic acid decomposes both the chloride and the hypochlorite in the bleaching powder. It follows from this that the action of hydrochloric acid on carbonates is a reversible one.

2. Ordinary moist air acts on solid bleaching powder, liberating at first both chlorine and hypochlorous acid, the former in much the larger amount. After a time nothing but chlorine is produced. When ordinary air is passed through a solution of bleaching powder, a mixture of hypochlorous acid and chlorine is swept out, at first in about equal amounts; but, as the experiment proceeds, the former diminishes, and the latter increases to about 90 per cent.

3. The action of chlorine on alkalis, like that of iodine and bromine, is a reversible one, as stated by von Tiesenholt. If the free lime in bleaching powder is removed, this causes the reverse action to proceed, and thus chlorine is liberated. This explains the action of ordinary air on bleaching powder. The reversibility of the action also explains the stimulating effect on bleaching which the addition of calcium chloride or of salt causes in a solution of bleaching powder.

4. In the ordinary processes of bleaching the active bleaching agent is probably free chlorine, hypochlorous acid playing only a minor part.

CCLXI.—*The Colour and Constitution of Diazonium Salts. Part III. The Diazo-derivatives of 2:7-Naphthylenediamine.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

ALTHOUGH the diazo-derivatives of the diamines of the benzene and diphenyl series have been extensively studied, owing largely to the circumstance that in many instances these products are of considerable industrial importance, yet comparatively little attention has been directed to the diazonium salts of the naphthylenediamines. Of the ten naphthylenediamines, three, namely, the 1:2-, 2:3-, and 1:8-compounds, are known to yield cyclic diazoimines (De Aguiar, *Ber.*, 1874, 7, 316; Friedländer and von Zakrzewski, *Ber.*, 1894, 27, 764; Morgan and Godden, this vol., p. 1707); the remaining seven give diazonium salts of varying degrees of stability (Ewer and Pick, D.R.-P. 45549, 45788; Badische Anilin- & Soda-Fabrik, D.R.P. 130475).

The case of 2:7-naphthylenediamine has recently been examined by Kauler in connexion with his theory of the stereochemical configuration of naphthalene and other polynuclear hydrocarbons. According to Kauler, the two nuclei present in naphthalene are bent round, using their two common carbon atoms as axis, so that the lateral extremities of the molecule represented by the positions 2:3 and 6:7 become contiguous. This supposed folding of the two nuclei would bring the two amino-groups of 2:7-naphthylenediamine into close proximity, and Kauler claims that the intimate association of these two groups is manifested by certain phenomena of steric hindrance which are advanced in support of his hypothesis * (*Annalen*, 1907, 351, 154; *Ber.*, 1907, 40, 3251).

It is asserted that the amino-groups of 2:7-naphthylenediamine exert a mutual inhibiting influence on each other, with the result that only one amino-group is diazotisable. In diazotising the hydrobromide or the hydrochloride of the diamine, Kauler and Karrer worked in acetic acid or alcoholic solution, and found that even

* It may be pointed out that Kauler's view is at variance with the ideas embodied in the Kekulé-Baeyer conception of the naphthalene molecule based on the tetrahedral carbon atom and the strain hypothesis, and also with the naphthalene model advocated by Pope and Barlow on crystallographic grounds. These conceptions, which may be termed respectively the functional and structural representations of naphthalene, although differing in many respects, concur in placing the 2:3 and 6:7-positions, not in contiguity, but at the lateral extremities of the molecule.

with excess of amyl nitrite only the monodiazonium salt was precipitated (*Ber.*, 1907, **40**, 3263).

This result is dependent, however, not on steric hindrance, but on experimental conditions. By operating with sodium nitrite or nitrosyl sulphate in moderately concentrated sulphuric acid, the authors have succeeded in diazotising completely both the amino-groups of the diamine. Probably the diazotisation occurs in two stages, and the isolation of the intermediate amino-diazonium salts by Kaufler and Karrer is dependent on the insolubility of these substances in the media employed.

EXPERIMENTAL.

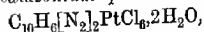
Naphthalene-2:7-bisdiazonium Sulphate (I), $\text{HSO}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{HSO}_4 \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{OH}$.

Recrystallised 2:7-naphthylenediamine (0.5 gram), melting at 160–161°, was dissolved in 2 c.c. of cold concentrated sulphuric acid, mixed with 1 gram of ice, and diazotised with 2 grams of nitrosyl sulphate, the mixture being cooled by further addition of 1 gram of ice. The cold filtered solution was carefully added to a mixture of two parts of ether and one of alcohol, and if the precipitated sulphate was viscous, more alcohol was added. The light yellow crystals thus obtained were washed with a mixture of ether and alcohol, and finally with ether; the yield of diazonium sulphate was 86 per cent. of the calculated quantity. The salt was appreciably soluble in alcohol, and when precipitated by ether in the presence of alcohol it retained a definite amount of the latter solvent, even after prolonged drying in the vacuum desiccator. The following analyses were carried out on different preparations which had been dried for varying periods:

| | | | | | | | | |
|---|------|--------|-------------------|-----|--------|------------------------|--------------------|------------------------|
| 0.2116 | gave | 0.2562 | CO_2 | and | 0.0562 | H_2O . | $\text{C}=33.02$; | $\text{H}=2.95$. |
| 0.1385 | " | 0.1688 | CO_2 | " | 0.0334 | H_2O . | $\text{C}=33.24$; | $\text{H}=2.68$. |
| 0.2020 | " | 0.2446 | CO_2 | " | 0.0514 | H_2O . | $\text{C}=33.02$; | $\text{H}=2.82$. |
| 0.0781 | " | 10.0 | c.c. N_2 | at | 22° | and | 756 | mm. $\text{N}=14.56$. |
| 0.2178 | " | 0.2570 | BaSO_4 . | | | | $\text{S}=16.20$. | |
| 0.1930 | " | 0.2356 | BaSO_4 . | | | | $\text{S}=16.76$. | |
| $\text{C}_{10}\text{H}_6\text{O}_8\text{N}_4\text{S}_2 \cdot \frac{1}{2} \text{C}_2\text{H}_5\text{O}$ requires $\text{C}=33.08$; $\text{H}=2.75$; $\text{N}=14.03$; | | | | | | | | |
| $\text{S}=16.04$ per cent. | | | | | | | | |

The bisdiazonium sulphate readily dissolved in water to a clear yellow solution, which was employed in the production of the following diazonium salts.

Naphthalene-2:7-bisdiazonium platinumchloride,



separated as a brownish-yellow, crystalline precipitate on adding

aqueous chloroplatinic acid to the solution of the bisdiazonium sulphate. The air-dried salt was not explosive, and could be warmed without decomposition:

0.1373 gave 0.0964 CO_2 and 0.0244 H_2O . $\text{C}=19.08$; $\text{H}=1.96$.

0.1760 „ 0.1243 CO_2 „ 0.0269 H_2O . $\text{C}=19.26$; $\text{H}=1.70$.

0.2170 „ 18.0 c.c. N_2 at 22° and 756 mm. $\text{N}=9.42$.

0.1542 „ 0.2122 AgCl . $\text{Cl}=34.02$.

0.1872 „ 0.0594 Pt . $\text{Pt}=31.73$.

0.1888 lost 0.0114 H_2O at $70-80^\circ$. $\text{H}_2\text{O}=6.04$.

$\text{C}_{10}\text{H}_6\text{N}_4\text{Cl}_6\text{Pt}\cdot 2\text{H}_2\text{O}$ requires $\text{C}=19.16$; $\text{H}=1.59$; $\text{N}=8.94$;

$\text{Cl}=34.02$; $\text{Pt}=31.15$; $\text{H}_2\text{O}=5.75$ per cent.

Naphthalene-2:7-bisdiazonium aurichloride, $\text{C}_{10}\text{H}_6(\text{N}_2\cdot\text{AuCl}_4)_2$, was obtained as a reddish-brown, crystalline precipitate on mixing aqueous solutions of chloroauric acid and the bisdiazonium sulphate. The aurichloride was very soluble in alcohol, and even dissolved slightly in ether:

0.1799 gave 0.0936 CO_2 and 0.0172 H_2O . $\text{C}=14.19$; $\text{H}=1.06$.

0.3118 „ 18.5 c.c. N_2 at 20.5° and 760 mm. $\text{N}=6.77$.

0.1290 „ 7.7 c.c. N_2 „ 20.5° „ 758 mm. $\text{N}=6.79$.

0.1620 „ 0.2170 AgCl . $\text{Cl}=33.15$.

0.1834 „ 0.0834 Au . $\text{Au}=45.47$.

$\text{C}_{10}\text{H}_6\text{N}_4\text{Cl}_6\text{Au}$ requires $\text{C}=13.95$; $\text{H}=0.69$; $\text{N}=6.51$; $\text{Cl}=33.02$;
 $\text{Au}=45.81$ per cent.

Naphthalene-2:7-bisdiazonium dichromate, $\text{C}_{10}\text{H}_6[\text{N}_2]_2\text{Cr}_2\text{O}_7$, separated either in reddish-brown leaflets or brown, nodular crystals on adding chromic acid or sodium dichromate to a dilute solution of the bisdiazonium sulphate:

0.2184 gave 24.4 c.c. N_2 at N.T.P. and 0.0824 Cr_2O_3 . $\text{N}=14.07$;
 $\text{Cr}=25.81$.

$\text{C}_{10}\text{H}_6\text{O}_7\text{N}_4\text{Cr}_2$ requires $\text{H}=14.07$; $\text{Cr}=26.13$ per cent.

The bisdiazonium dichromate is extremely explosive, and detonates with a bright flash when gently heated or even on rubbing.

The bisdiazonium sulphate gave rise to sparingly soluble diazoborivatives when added to aqueous solutions of alkali vanadates, molybdates, and tungstates.

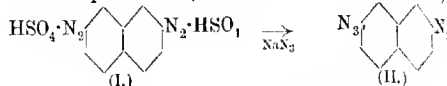
*The Sandmeyer Reaction with the Bisdiazonium Salts of
2:7-Naphthylenediamine.*

The purified naphthalene-2:7-bisdiazonium sulphate (carefully freed from any excess of nitrous acid) was dissolved in water and added to a hydrochloric acid solution of cuprous chloride. 2:7-Dichloronaphthalene separated immediately, and was purified by sublimation, when it melted at $114-115^\circ$, and did not depress the

melting point of a specimen prepared from naphthalene-2:7-di-sulphonic acid, for which the authors are indebted to Professor Armstrong.

This Sandmeyer reaction gave the same result when repeated with the other bisdiazonium salts of 2:7-naphthylenediamine.

2:7-Bistriazonaphthalene (Naphthylene-2:7-bisazoimide),



2:7-Bistriazonaphthalene (II) was obtained as a brownish-white precipitate on adding sodium azide to a well-cooled aqueous solution of the bisdiazonium sulphate which had been carefully freed from nitrous acid. The product crystallised from petroleum (b. p. 60–80°) in almost colourless leaflets or tabular prisms, which reddened on exposure to light; it melted at 98°:

0.1984 gave 0.4158 CO₂ and 0.0569 H₂O. C=57.14; H=3.18.

0.0784 „ 27.0 c.c. N₂ at 22° and 760 mm. N=39.84.

C₁₀H₆N₆ requires C=57.14; H=2.85; N=40.00 per cent.

2:7-Bistriazonaphthalene has a characteristic odour, recalling that of β-ethoxynaphthalene; it can be partly decolorised by boiling with methyl alcohol and animal charcoal, and crystallises from this solvent in very pale pink plates. Cold concentrated sulphuric acid decomposes the bistriazo-compound with effervescence.

The decomposition of the bisdiazonium sulphate with sodium azide is practically quantitative, and as 2:7-bistriazonaphthalene is only very sparingly soluble in water, its amount can be determined:

0.1398 C₁₀H₆(N₂·HSO₄)₂·½C₂H₅·OH gave 0.0741 C₁₀H₆(N₃)₂, melting at 98°, whereas the calculated amount is 0.0736.

The aqueous filtrate from the precipitated bistriazo-compound which contained the alcohol of crystallisation of the bisdiazonium sulphate, gave a distinct iodoform reaction, thus confirming the analytical data for this salt.

THEORETICAL CONSIDERATIONS.

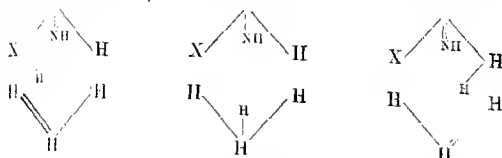
The fact that the 2-aminonaphthalene-7-diazonium salts isolated by Kautler and Karrer (*loc. cit.*) and the naphthalene-2:7-bis-diazonium sulphate described above are yellow compounds afford additional evidence in favour of the view that diazonium salts of normal constitution display colour when their diazo-complexes are associated with polynuclear hydrocarbon radicles (compare this vol. p. 1691).

The successive diazotisation of 2:7-naphthylenediamine salts in

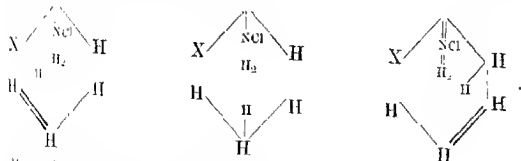
two stages is of interest in connexion with the authors' views on the constitution of diazonium salts.

In the first place, it should be noted that all the available evidence amply supports the assumption that the diazotisability of a base depends on the association of its amino-group with an unsaturated organic complex. This complex need not necessarily be aromatic or even cyclic, but it is, apparently, essential that this group should be unsaturated, for hitherto no amine possessing a fully saturated radicle has ever been diazotised. The existence of a certain degree of residual affinity is a necessary condition for the production of diazonium salts.

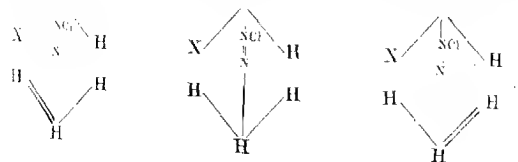
In the aromatic series this residual affinity is supplied by the fourth valency of each carbon atom of the six-membered rings, and the chemical properties which characterise aromatic amines (oxidation, diazotisation, etc.) may be supposed to arise from the interaction of these bases in their tautomeric forms (compare Cain, *Trans.* 1907, 91, 1051).



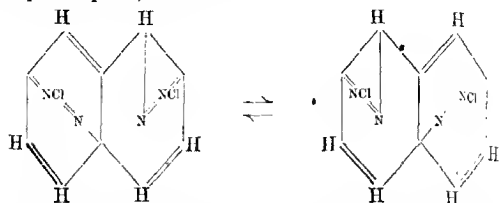
It cannot be too strongly emphasised that diazotisation is a process which takes place only with the undissociated salt of an amine, and not with the base itself. Accordingly, the nitrous acid reacts with the salts (for example, the hydrochloride) of the base in the following tautomeric forms:



Regarded in this way, diazotisation, which consists in the replacement of three labile hydrogen atoms by nitrogen, leads naturally to the formation of three tautomeric forms of the diazonium chloride:



In the special case of the salts of 2:7-naphthylenediamine, the progressive diazotisation arises probably from the circumstance that the two diazonium complexes represent two phases of the diazo-configuration. If the first formed diazonium complex has the para-hemiquinoid structure, then the second will be in the ortho-hemiquinoid phase, and vice versa:



The foregoing hypothesis of the constitution of diazonium salts is based on the assumption that the aromatic amines and their salts are able to react in the tautomeric imino-forms, a change which is possible only when the organic complex associated with the amino-group is unsaturated.

Tautomeric change to the imino-form is possible in the following non-aromatic amines, all of which have manifested to some extent the property of diazotisability:

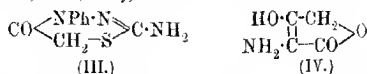
The aminotriazoles (Thiele and Manchot, *Annalen*, 1898, 303, 33):



4-Amino-1:5-diphenyl-1:2:3-triazole (Dimroth, Frisoni, and Marshall, *Ber.*, 1906, 39, 2925) and aminoantipyrine (Knorr and Stolz, *Annalen*, 1896, 293, 67), represented respectively by formulæ I and II:

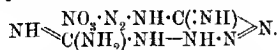


Aminophenylprithiazinone (Harries and Klamt, *Ber.*, 1900, 33, 1158) and aminotetronic anhydride (Wolff and Lüttringhaus, *Annalen*, 1900, 312, 133), with formulæ III and IV:



In addition to these non-aromatic amines, in which the amino-group is associated with a cyclic structure, an interesting extension of the diazo-reaction has recently been discovered by K. A. Hofmann, H. Hock, and R. Roth (*Ber.*, 1910, 43, 682, 1087), who find that under certain conditions aminoguanidine furnishes diazonium salts

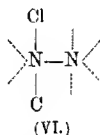
derived, however, not from salts of the base itself, but from a more complex molecule containing two guanidine residues and having a greater degree of unsaturation. The diazonium nitrate, for example, is represented by the formula:



Even in this compound it is possible to discern in the three double linkings a certain analogy to the aromatic diazonium salts.

A further extension of the hypothesis that the diazotisability of an amine depends on the presence in its molecule of an unsaturated group may be put forward to explain why the tendency to form diazonium salts is greatest among aromatic amines.

In the aromatic series, unsaturation of the hydrocarbon radicle is due to the fourth valency of each carbon atom of a six-membered ring. In the diazonium complex, three valencies of one of the two nitrogen atoms are employed as follows: one furnishes the attachment to an acid radicle; another links the diazo-group with a carbon atom of the ring; and the third forms one of the bonds of attachment to the second nitrogen atom. Regarding nitrogen as always potentially quinquevalent, an assumption which is justified by the position of this element in the periodic classification, then the diazonium complex itself, like the aromatic nucleus, has also an unsaturation represented by six valencies. These two sets of six valencies, representing respectively the residual affinities of the aromatic and diazonium complexes, are indicated by dotted lines in formulæ V and VI, the first of which is the well-known centric formula:



The authors' view is that maximum stability of the diazonium salt results when the residual affinities of the organic radicle and the diazonium complex satisfy each other to the fullest extent. In an aromatic monodiazonium salt, the residual affinity of the diazo-group is available for saturating the six fourth valencies of the aromatic ring.

This conception of the constitution of diazonium salts suggests, also, an explanation of the following facts: (1) the relative instability of the bisdiazonium salts of homonuclear aromatic diamines; (2) the difficulty sometimes experienced in diazotising completely the salts of these diamines.

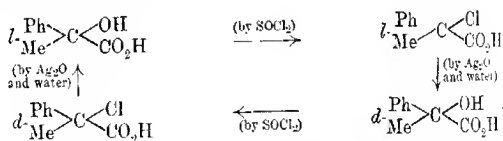
The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CCLXII.—*Experiments on the Walden Inversion. Part VI. Conversion of the Optically Active α -Hydroxy- α -phenylpropionic Acids into α -Chloro- α -phenylpropionic Acids.*

By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

THE authors showed in a former paper (Trans., 1910, 97, 1016) that when *l*- α -hydroxy- α -phenylpropionic acid was acted on by thionyl chloride at the ordinary temperature there was no evidence that the carboxyl group had been attacked, whereas the hydroxy-group in direct attachment to the asymmetric carbon atom was displaced by the chlorine atom with great readiness.* By this method *l*- and *d*- α -chloro- α -phenylpropionic acids were easily obtained in a state of optical purity, and the interconversion of the optically active α -hydroxy- α -phenylpropionic acids was brought about by aid of the Walden inversion, thus:

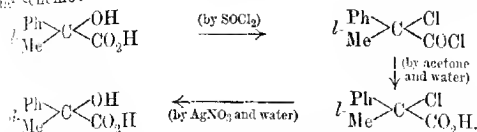


The results obtained by a further study of this subject are placed on record in the present communication.

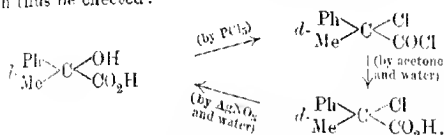
When the action of thionyl chloride on *l*- α -hydroxy- α -phenylpropionic acid is conducted in such a manner that both hydroxy-groups are displaced by chlorine, the resulting chloro-acid chloride is *laevorotatory*, and on decomposition with acetone containing a little water it gives *l*- α -chloro- α -phenylpropionic acid. The inter-

* Later, Selié (Ber., 1910, 43, 2471) observed that benzoic acid is converted into diphenylchloroacetic acid in a similar manner when its solution in carbon tetrachloride is acted on by thionyl chloride at the ordinary temperature.

inversion of the active hydroxy-acids can be carried out according to the scheme:

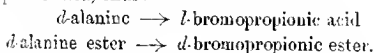


On the other hand, when *l*- α -hydroxy- α -phenylpropionic acid is acted on by phosphorus pentachloride, a change of sign of rotation occurs: the chloro-acid chloride is in this case *dextro*rotatory, and gives *d*-chloro- α -phenylpropionic acid when it is decomposed by aqueous acetone. When the chlorine in the latter product is displaced by the hydroxy-group by aqueous silver nitrate, the parent α -hydroxy- α -phenylpropionic acid is regenerated. The following cycle can thus be effected:

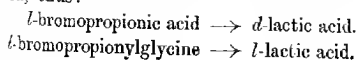


Thionyl chloride and phosphorus pentachloride thus behave differently towards *l*- α -hydroxy- α -phenylpropionic acid, inasmuch as the former gives the *l*-chloro-acid, whereas the latter gives the *d*-chloro-acid. The action of phosphorus pentachloride is accompanied with a large amount of racemisation.

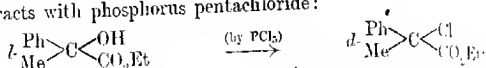
In the course of his work on the Walden inversion, E. Fischer (*Ber.*, 1907, 40, 489) found that *l*-bromopropionic acid is formed from *d*-alanine by the action of nitrosyl bromide, this action being probably abnormal; when the ester of *d*-alanine, however, is acted on by nitrosyl bromide, the resulting compound is the ester of *d*-bromopropionic acid, thus:



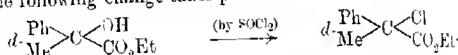
The conclusion is drawn that the same reagent (nitrosyl bromide) can act on closely-related substances (for example, acid and ester), in one case normally and in the other case abnormally. This conclusion was borne out when the behaviour of nitrosyl chloride towards active leucine (and its ester) and active aspartic acid (and its ester) was examined. Again, silver oxide, which apparently behaves abnormally in Walden's experiments with the malic acids, is used to produce either *d*- or *l*-lactic acid from *l*-bromopropionic acid, thus:



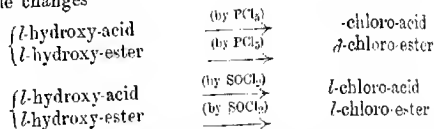
Bearing these results of Fischer in mind, we decided to investigate the action of phosphorus pentachloride and thionyl chloride respectively on the ethyl ester of active α -hydroxy- α -phenylpropionic acid in the hope of throwing some light on the problem as to which of these agents acts abnormally on the hydroxy-acid. The following change, which is accompanied by a large amount of racemisation, takes place when ethyl *l*- α -hydroxy- α -phenylpropionate interacts with phosphorus pentachloride:



Unfortunately, the action of thionyl chloride on ethyl *d*- α -hydroxy- α -phenylpropionate does not proceed smoothly, but we have evidence that the following change takes place:

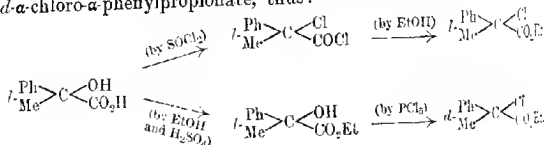


When the changes



are contrasted, it will be seen that no conclusion can be drawn from them as to which of the agents, thionyl chloride or phosphorus pentachloride, causes the Walden inversion when it acts on the hydroxy-acid.

It was obviously desirable to prove that the *l*-chloro-acid corresponds in configuration with the *l*-chloro-ester. This was done by showing that the *l*-chloro-acid chloride (which gives the *l*-chloro-acid on treatment with aqueous acetone) is converted into the *l*-chloro-ester on addition to ethyl alcohol, the sign of rotation remaining unchanged. It is accordingly possible to convert *l*- α -hydroxy- α -phenylpropionic acid into either ethyl *l* or ethyl *d*- α -chloro- α -phenylpropionate, thus:



EXPERIMENTAL.

Action of Thionyl Chloride on l- α -Hydroxy- α -phenylpropionic acid

A mixture of *l*- α -hydroxy- α -phenylpropionic acid (6 grams, prepared by the resolution of the *r*-acid with morphine (loc. cit.

and thionyl chloride (20 grams) was kept at the ordinary temperature for two days, and then heated at 80° for one hour. Five grams of a *dextrorotatory* acid chloride boiling at $108-110^{\circ}/10$ mm. were obtained. It was added to a mixture of acetone (20 c.c.) and water (1 c.c.), and after a day the solvent was removed at the ordinary temperature under diminished pressure. The crude chloro-acid (3 grams) was crystallised once from light petroleum, when the pure acid (*loc. cit.*) was obtained, melting at $71-72^{\circ}$, and having the following specific rotation in benzene solution:

$$l=2, c=7.188, \alpha_D-3.78^{\circ}, [\alpha]_D-26.3^{\circ}.$$

This acid gave a *dextrorotatory* mixture of α -hydroxy- α -phenylpropionic acids when the displacement of chlorine was effected by acid of aqueous silver nitrate.

It is thus possible to prepare optically pure *l*- α -chloro- α -phenylpropionic acid even when the temperature of the action with thionyl chloride is raised so that the carboxyl group of the hydroxy-acid is displaced.

The *levorotation* of the chloro-chloride, prepared from 6 grams of the *l*-hydroxy-acid and 28 grams of thionyl chloride under temperature conditions somewhat different from the preceding, was confirmed. One gram of the chloro-chloride was added to 7 c.c. of acetone, and the solution gave $\alpha_D-4.5^{\circ}$ in a 1-dm. tube.

Action of Phosphorus Pentachloride on l- and d- α -Hydroxy- α -phenylpropionic Acids.

A mixture of *l*- α -hydroxy- α -phenylpropionic acid (12 grams) and the calculated amount of phosphorus pentachloride (30 grams) was maintained at 15° for thirty minutes, by which time the vigorous evolution of hydrogen chloride had subsided. On heating to 70° , a brisk action again took place; the temperature was raised from 70° to 100° within thirty minutes, and finally maintained at 100° for one hour. The action of the phosphorus pentachloride apparently took place in two distinct stages. The phosphoryl chloride was removed, and the residual oil fractionated under diminished pressure. Six grams of a colourless oil, boiling at $113-115^{\circ}/15$ mm., were obtained. This chloro-acid chloride was *dextrorotatory*, giving $\alpha_D+3.10^{\circ}$ in a 1-dm. tube, and its solution in acetone was also *dextrorotatory*. It was added to a mixture of acetone (20 c.c.) and water (1 c.c.). Next day, the solvent was removed at the ordinary temperature under diminished pressure, and the residual solid drained on porous earthenware. It amounted to 4 grams, melted at $70-75^{\circ}$, and gave the following value in benzene solution:

$$l=2, c=12.7, \alpha_D+0.56^{\circ}, [\alpha]_D+2.2^{\circ}.$$

Found, Cl=19.2. Calc. Cl=19.3 per cent.

The resulting acid was thus a mixture of *d*- and *r*- α -chloro- α -phenylpropionic acids, and a change of sign of rotation accordingly took place during the displacement of the chlorine by the hydroxy-group under the following conditions. The acid was shaken for four hours at the ordinary temperature with a solution of 5 grams of silver nitrate in 20 c.c. of water, and the mixture was then boiled for one minute and filtered. The hydroxy-acid was extracted with ether. It melted at 88–90°, was free from chlorine, and was laevorotatory. In ethyl-alcoholic solution:

$$l=4, c=9.58, \alpha_D - 0.67^\circ, [\alpha]_D - 1.7^\circ.$$

The action of phosphorus pentachloride (25 grams) on *d*- α -hydroxy- α -phenylpropionic acid (10 grams) was also studied under conditions similar to the preceding. The chloro-acid chloride was in this case laevorotatory. On decomposition with aqueous acetone it gave a mixture of *l*- and *r*- α -chloro- α -phenylpropionic acids.

Conversion of l- α -Chloro- α -phenylpropionyl Chloride into Ethyl l- α -Chloro- α -phenylpropionate.

The laevorotatory α -chloro- α -phenylpropionyl chloride, prepared from *l*- α -hydroxy- α -phenylpropionic acid (10 grams) and thionyl chloride (28 grams), was added to ethyl alcohol and the product fractionated. The ester was a laevorotatory oil; it amounted to 4 grams, boiled at 131–132°/18 mm., and gave the following values:

$$l=1, \alpha_D^{20} - 6.30^\circ, D_4^{20} 1.124, [\alpha]_D^{20} - 5.6^\circ.$$

Found, Cl=16.8. $C_{11}H_{13}O_2Cl$ requires Cl=16.7 per cent.

We have no evidence that this ester was optically pure, and it is necessary to bear in mind that partial racemisation occurs very frequently when the alcoholic hydroxy-group of an optically active hydroxy-carboxylic acid is displaced by halogen.

It appeared from the following experiment that this ester corresponds in configuration with *l*- α -chloro- α -phenylpropionic acid. The ester (3 grams) was added to 25 c.c. of *N*-aqueous silver nitrate, and maintained at the ordinary temperature for twenty-four hours. The silver chloride was removed, and the filtrate boiled with aqueous potassium hydroxide until all the oil had disappeared. The resulting α -hydroxy- α -phenylpropionic acid obtained by acidification and extraction with ether amounted to 2 grams, melted at 84–89°, and was dextrorotatory in ethyl-alcoholic solution:

$$l=2, c=18.48, \alpha_D + 1.33^\circ, [\alpha]_D + 3.6^\circ.$$

*Action of Phosphorus Pentachloride and of Thionyl Chloride on the
(Optically Active Ethyl α -Hydroxy- α -phenylpropionates.*

Ethyl l- α -hydroxy- α -phenylpropionate, $\text{OH}\cdot\text{CMePh}\cdot\text{CO}_2\text{Et}$, prepared by the esterification of *l*- α -hydroxy- α -phenylpropionic acid by ethyl alcohol and sulphuric acid, is an oil boiling at $127^\circ/12$ mm.:

d_{20}^{20} gave 0.3322 CO_2 and 0.0865 H_2O . $\text{C}=68.1$; $\text{H}=7.3$.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires $\text{C}=68.0$; $\text{H}=7.3$ per cent.

It has $D_D^{20} 1.097$ and $\alpha_D^{20} -29.24^\circ$ ($l=1$); whence $[\alpha]_D^{20} -26.7^\circ$.

When this ester is acted on by phosphorus pentachloride, the resulting ethyl α -chloro- α -phenylpropionate is *dextrorotatory*, but it is impossible to prevent a large amount of racemisation taking place in this change. Powdered phosphorus pentachloride (7 grams) was added gradually within an interval of one hour to the hydroxy-ester (6 grams). After three hours at the ordinary temperature the product was warmed at 30° for a few minutes, when no further action was perceptible. It was then treated with ether and ice, and the ethyl α -chloro- α -phenylpropionate isolated as an oil boiling at $138\text{--}139^\circ/28$ mm.:

Found, $\text{Cl}=16.5$. $\text{C}_{11}\text{H}_{13}\text{O}_2\text{Cl}$ requires $\text{Cl}=16.7$ per cent.

The ester had $\alpha_D^{20} +1.10^\circ$ in a 1-dm. tube.

On decomposing it with a slight excess of 1.03*N*-aqueous sodium hydroxide, the displacement of the chlorine by the hydroxy-group of course accompanied the saponification; the product of the action was *ra*-hydroxy- α -phenylpropionic acid.

Although attempts to prepare ethyl *dl*- α -chloro- α -phenylpropionate in a state of even approximate purity from ethyl *dl*- α -hydroxy- α -phenylpropionate (b. p. $124\text{--}125^\circ/10$ mm.) and thionyl chloride met with no success, it was nevertheless decided to examine the action of thionyl chloride on the optically active hydroxy-esters. The material used for this purpose was the dextrorotatory mixture of *l*- and *r*- α -hydroxy- α -phenylpropionic acids obtained from the mother liquors resulting from the morphine resolution of the *r*-acid. It was esterified by ethyl alcohol and sulphuric acid, and the ester obtained had $\alpha_D^{20} +11^\circ$ in a 1-dm. tube. Twelve grams of this product remained for seven days at the ordinary temperature after having been mixed with 14 grams of thionyl chloride. The liquid was then heated for twenty hours at $50\text{--}60^\circ$, and for five hours longer at $60\text{--}70^\circ$, but the action was apparently not quite complete even under these conditions. The product was fractionated, and an oil boiling at $138\text{--}141^\circ/25$ mm. was obtained; it was *dextrorotatory*, giving $\alpha_D^{20} +1.50^\circ$ in a 1-dm. tube. It contained, however, only 11.7 per cent. of chlorine. We were able to draw the conclusion,

however, from the following experiment that *d*- α -chloro- α -phenyl propionate was actually present in this impure product. The chlorine in it was first displaced by aqueous silver nitrate, and the product then saponified with aqueous potassium hydroxide. The resulting potassium salt was *laevorotatory* in aqueous solution, and the α -hydroxy- α -phenylpropionic acid obtained from it was also *laevorotatory*. This result was confirmed by a second experiment.

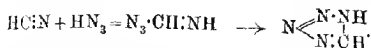
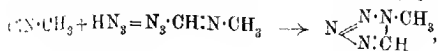
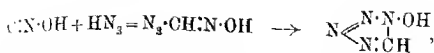
BIRKBECK COLLEGE,
LONDON, E.C.

CCLXIII.—*The Triazo-group. Part XV. Triazo-ethylene (Vinylazoisimide) and the Triazothyl Halides.*

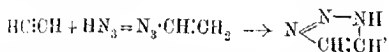
By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

MANY cases have now been placed on record in which the atoms composing a triazo-group in the neighbourhood of an unsaturated linking have lent themselves to the formation of a cycloid, owing to a change involving saturation of this linking by the members of the azoisimide nucleus. As recent examples of this principle may be quoted the spontaneous transformation of allylazoisimide into an isomeric diazcamino-compound (*Trans.*, 1908, **93**, 1174), whilst an attempt to prepare benzhydroximic azide by interaction of the chloride and sodium azide led to 1-hydroxy-5-phenyltetrazole (*Trans.*, 1909, **95**, 183; compare also Wieland, *Ber.*, 1909, **42**, 4199).

In the cases mentioned above, and in others which might be indicated, the environment favourable to the display of additive functions on the part of the triazo-group is intramolecular. Whether it is necessarily so cannot be stated with confidence, because, although striking examples of apparently intermolecular addition have been furnished quite recently by Palazzo and Oliveri-Mandalà (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 218, 228), who found that hydrazoic acid converts fulminic acid and methyl-carbylamine into 1-hydroxytetrazole and 1-methyltetrazole respectively, whilst Dimroth and Fester (*Ber.*, 1910, **43**, 2219) showed that tetrazole itself is obtainable by the interaction of hydrazoic and prussic acids, it is nevertheless possible that these changes actually depend on preliminary addition of H and N₃ to unsaturated atoms, and that it is the resulting triazo-compound which undergoes intramolecular rearrangement, as follows:



In addition to the experiment just mentioned, Dimroth and Forster caused hydrazoic acid to act on acetylene, and although 1,2:3-triazole was obtained therefrom, they do not classify this change with the foregoing ones, as depending on the intermediate formation of vinylazoisimide,

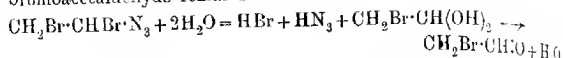


because phenylazoisimide is converted into 1-phenyl-2:3-triazole by the action of acetylene. As we have been engaged for some time in experiments leading to the preparation of vinylazoisimide, we think it may be of interest to put forward a description of this substance, which was isolated with the object of studying its tendency to undergo the above rearrangement.

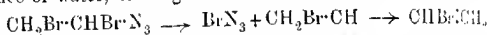
The first experiments in the direction indicated were begun more than two years ago in continuation of the work on allylazoisimide. Attempts were made to bring vinyl bromide into double decomposition with sodium azide, but there was not any evidence of the change having taken place; in spite of the readiness with which usually the triazo-group may be substituted for halogen in aliphatic compounds, the failure was not surprising, as it is well known that halogen attached to unsaturated carbon takes part in such reactions with the greatest difficulty. The preparation of triazoethyl alcohol (Trans., 1908, 93, 1865), however, suggested the possibility of arriving at triazoethylene (vinylazoisimide) by the withdrawal of halogen hydride from a triazoethyl halide. Accordingly, triazoethyl alcohol was converted into triazoethyl bromide by the action of phosphorus tribromide, and then by double decomposition with potassium iodide, triazoethyl iodide was prepared from the bromide; on treating with alcoholic potassium hydroxide on these compounds, they were readily deprived of halogen hydride without affecting the triazo-group.

Triazoethylene is a pale yellow liquid, heavier than water, boiling at 129°, and having an odour suggesting that of ethylene itself. It decolourises bromine water without delay, forming a heavy, oily diimide. At one time we entertained the hope that it might be possible to withdraw the elements of hydrogen bromide from this substance in such a way as to produce triazoacetylene, the copper

derivative of which would probably rank among violent explosives, but it was soon found that the dibromide itself is a dangerous material, and, moreover, breaks up in an interesting manner under the influence of water. When suspended therein, the oil rapidly disappears, hydrobromic and hydrazoic acids being set free, while bromoacetaldehyde remains dissolved:

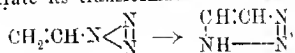


So far as we know, the dibromide of triazoethylene is the first compound in which a triazo-group is attached to an atom of carbon which carries also a halogen, and its peculiar susceptibility towards water explains the subsidiary decomposition which has always been observed to accompany the production of a bistriazo-compound from the double decomposition of sodium azide and a dihalogen derivative of the aliphatic series in which both halogen atoms are attached to the same atom of carbon (Trans., 1908, 93, 1070; also this vol. pp. 126 and 1360). We have not attempted to isolate and distill the substance, because a brief experience of $\alpha\alpha$ -bistriazoethane, which exploded with great violence at the laboratory temperature, apparently spontaneously, renders it most probable that $\alpha\beta$ -dibromo- α -triazoethane would behave in the same way. This seems the more likely to take place in view of the possibility that the decomposition of triazoethylene dibromide might follow a different course in the absence of water, leading to bromoazoimide:



Since Raschig has shown (Ber., 1908, 41, 4194) that chloroazidoimide is frightfully explosive, the foregoing possibility is discouraging to a further investigation of $\alpha\beta$ -dibromo- α -triazoethane.

The original purpose with which triazoethylene was prepared, namely, to illustrate its transformation into triazole:



has not been fulfilled, the substance having shown itself to be surprisingly stable. After being heated with dilute alcohol under reflux during twelve hours, a considerable proportion was found to have survived, and although the remainder had changed into a dark brown substance, the presence of triazole could not be established. Furthermore, on heating an alcoholic solution in a sealed tube during twelve hours at 100–110°, there was produced a dark brown liquid having the odour of a carbylamine, and giving a precipitate with mercuric chloride, but again it was not found possible to recognise triazole.

The pale yellow colour of triazoethylene is an interesting feature of the compound, and appears to be a genuine property, because

it has been noticed in every specimen, whether prepared from triazoethyl iodide or bromide. It is doubtless due to the concentration of unsaturated atoms in a small molecule, and although not so intense as that of diazomethane, it is nevertheless quite distinctive. The comparatively high boiling point was not expected, because the recorded boiling points of vinyl chloride and of vinyl bromide are -15° and $+16^{\circ}$ respectively, and without having made a study of the subject, we were under the impression that, whilst the boiling point of an aliphatic chloro-derivative is unquestionably lower than that of the corresponding triazo-compound, the latter would be more volatile than the brominated substance. As it is often a matter of considerable practical importance to be able to predict, roughly, the boiling point of a new triazo-compound from that of its haloid parent, we have taken afresh the boiling point of several typical aliphatic azoimides described in previous papers, side by side with those of the corresponding bromo-derivatives. The results show conclusively that the triazo-group exerts an elevating effect on the boiling point greater than that of the bromine atom.

| | | B. p. | Mm. |
|---------------------------------------|--|-------|-----|
| Vinyl bromide | CH_2CHBr | 16' | 750 |
| Vinylazomide | CH_2CHN_3 | 26 | 760 |
| Ethyl-ene dibromide | $\text{CH}_2\text{BrCH}_2\text{Br}$ | 37 | 20 |
| Triazoethyl bromide | $\text{CH}_2\text{BrCHN}_3$ | 49 | 20 |
| Ethyl α -bromopropionate | $\text{CH}_3\text{CHBrCO}_2\text{Et}$ | 61 | 16 |
| .. α -triazopropionate | $\text{CH}_3\text{CHN}_3\text{CO}_2\text{Et}$ | 70 | 16 |
| .. α -bromoisobutyrate | $\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}_2\text{Et}$ | 62 | 16 |
| .. α -triazoisobutyrate | $\text{CN}_3\text{CH}(\text{CH}_3)\text{CO}_2\text{Et}$ | 71 | 16 |
| .. α -bromoisovalerate | $\text{CH}(\text{CH}_3)_2\text{CHBrCO}_2\text{Et}$ | 79 | 16 |
| .. α -triazoisovalerate | $\text{CH}(\text{CH}_3)_2\text{CHN}_3\text{CO}_2\text{Et}$ | 82 | 16 |

The relationship between the triazo-group and the chlorine atom as regards their effect on the boiling point is revealed by the following data:

| | | B. p. | Mm. |
|--|--|---------------|------|
| Vinyl chloride | CH_2CHCl | -15° | 760 |
| Vinylazomide | CH_2CHN_3 | 26 | 760 |
| 2-(2-triazoethyl) alcohol | $\text{CH}_2\text{ClCH}_2\text{OH}$ | 44 | 20 |
| 2-Triazoethyl | $\text{CH}_2\text{N}_3\text{CH}_2\text{OH}$ | 73 | 20 |
| Ethyl chloroformate | ClCO_2Et | 93 | 760 |
| .. triazoformate | $\text{N}_3\text{CO}_2\text{Et}$ | 114 | 760 |
| .. chloroacetate | $\text{CH}_3\text{ClCO}_2\text{Et}$ | 52 | 20 |
| .. triazoacetate | $\text{CH}_3\text{N}_3\text{CO}_2\text{Et}$ | 70 | 20 |
| Methyl α -chloromethylacetate | $\text{CH}_3\text{COClCH}_2\text{CO}_2\text{Me}$ | 76 | 13 |
| .. α -triazomethylacetate | $\text{CH}_3\text{CON}_3\text{CH}_2\text{CO}_2\text{Me}$ | 76 | 0.66 |

We have not, as yet, been very successful in attempts to utilise triazoethyl iodide as a triazo-ethylating agent. Triazoethyl chloride has been obtained by heating the iodide with dry mercuric chloride, and in this connexion it is worth noting that the bromide remains unchanged when treated with the mercury salt under similar conditions. *iso*-Nitrosocamphor was transformed into an oily triazo-

ethyl derivative when heated with triazoethyl iodide and silver oxide in dry ether, but an attempt to prepare bistriazoethyl ether by heating a mixture of triazoethyl alcohol and iodide with dry silver oxide on the water-bath led to the recovery of unaltered triazoethyl alcohol after five days. This is the more curious because the action of ethyl iodide on triazoethyl alcohol in presence of silver oxide leads without difficulty to triazoethyl ether, $C_2H_5 \cdot O \cdot CH_2 \cdot CHN_3$. Lastly, we have not been able to produce triazoethylcarbimide by the action of triazoethyl iodide on lead or silver cyanate, whilst the interaction of triazoethyl iodide and silver cyanide, although producing an odour of carbylamine, was too far from complete to admit of isolating any definite products.

EXPERIMENTAL.

Triazoethylenc (Vinylazoisimide), $CH_2 \cdot CHN_3$.

The alcoholic potassium hydroxide used for withdrawing halogen hydride from the triazoethyl halides was a solution of 5 grams in 20 grams of water, mixed with 25 grams of absolute alcohol. This was heated on steam in a generating flask, into which was fitted a dropping-funnel and a reflux double-surface condenser; from the latter, connexion was made to a small, dry flask, thence to a U-tube filled with calcium chloride, and finally to a large test-tube surrounded by a freezing-mixture. The temperature of the water in the condenser having been adjusted to 30° , 5 grams of triazoethyl iodide was admitted drop by drop into the alcoholic potassium hydroxide at the temperature of boiling alcohol, when a pale yellow liquid gradually accumulated in the small flask between the generator and the U-tube. All the iodide having been added, the liquid was boiled during fifteen minutes, when it was found that the cooled tube also contained some yellow liquid, and this, being presumably free from alcohol and water, was regarded as pure triazoethylenc, and found to boil at $26^\circ/760$ mm. Although this experiment has been made several times, and triazoethyl bromide has been substituted for the iodide, it has always been observed that the liquid in both condensing vessels is pale yellow, and that the colour does not vary in depth; it therefore seems safe to conclude that this feature is not due to some impurity. Reference has been made to the absence of any conclusive evidence that triazoethylenc changes into triazole; in addition to the experiments towards this end which have been already described, a solution of triazoethylenc in petroleum was left in a stoppered vessel exposed to light during many days without giving the faintest indication of triazole; on allowing the solvent to evaporate, the odour of a carbylamine was noticeable.

The dibromide of triazoethylene was prepared by adding ice-cold dilute water to a well-cooled suspension of the substance in water, the colour of the halogen being immediately destroyed, whilst the liquid vinylazoimide changed to a heavy, viscous oil. It is necessary to be most cautious in adding the halogen, because on one occasion a drop of bromine was admitted by accident to the vessel containing the triazo-compound, and led to a violent explosion, although the amount of material involved could not have exceeded 1 gram, and this was diluted with 20 c.c. of water. On allowing the dibromide to remain in contact with water, it rapidly disappeared, and the liquid was found to contain hydrazoic and hydrobromic acids; moreover, it restored the colour to Schiff's reagent, and when mixed with ammoniacal silver oxide and filtered, the liquid quickly deposited silver on warming. In order to make sure that the decomposition of triazoethylene dibromide by water does not follow the possible alternative course, that, namely, leading to bromoazoimide and vinyl bromide, a specimen of vinylazoimide was converted into the dibromide with a deficit of bromine, and at once treated with dilute sodium hydroxide, in the expectation that if bromoazoimide were formed, it would behave towards alkali in the manner that characterises chloroazoimide, and that alkali hypobromite would be produced; we were able to show that hypobromite is not formed, and therefore conclude that the decomposition proceeds only in the reaction of hydrobromic and hydrazoic acids along with bromoacetaldehyde.

The interaction of triazoethylene and concentrated sulphuric acid is mild, gas being evolved slowly, but brisk effervescence occurs with a solution of stannous chloride in hydrochloric acid. The conclusion that alcoholic potassium hydroxide is without action on the substance may be drawn from the fact that on evaporating to dryness the liquid contained in the generating flask, no trace of alkali azide was to be found.

β-Chloro-*α*-triazothane (Triazoethyl Chloride), $N_3 \cdot CH_2 \cdot CH_2Cl$.

The first attempts to prepare this material were made by adding triazoethyl alcohol dissolved in absolute ether to the calculated amount of phosphorus pentachloride covered with the same solvent; considerable action took place, and was increased by heating under reflux, but the yield of triazoethyl chloride, being only 2 grams from 20 grams of the alcohol, was too disappointing to encourage the adoption of this method. Thionyl chloride acts vigorously on triazoethyl alcohol, but, as might be expected, gives a product which appears to be triazoethyl sulphite, and triazoethyl chloride could not be detected, whilst the effect of passing dry hydrogen chloride

into a suspension of anhydrous zinc chloride in triazoethyl alcohol was to liberate hydrazoic acid. It was not until triazoethyl iodide became available that the preparation of the chloride was possible.

Twenty grams of triazoethyl iodide, mixed with 32 grams of dried mercuric chloride, were heated at 100° during three hours in a small distilling flask, from which the product was then boiled under 25 mm. pressure, 10 grams, or 90 per cent. of the theoretical amount, being obtained; on re-distillation under the same pressure, the substance boiled steadily at 45°:

0.0874 gave 30.9 c.c. N_2 at 24° and 751 mm. $N = 39.16$.

0.2709 „ 0.3642 AgCl. $Cl = 33.25$.

$C_2H_4N_3Cl$ requires $N = 39.81$; $Cl = 33.65$ per cent.

The substance is limpid and colourless, having a pleasant odour suggesting that of chloroform; the density is 1.2885/24°. The action with a solution of stannous chloride in hydrochloric acid is sluggish, gas being evolved only on warming the liquids; the effervescence with concentrated sulphuric acid becomes brisk on stirring, but the triazo-group appears to be indifferent towards alkalis, which only liberate triazoethylene. The chloride does not lose its halogen completely when heated with boiling alcoholic silver nitrate, as is the case with the other triazoethyl halides, and the above estimation of chlorine was made by heating in alcohol with 30 per cent. aqueous potassium hydroxide, followed by precipitation with silver nitrate in the solution acidified by nitric acid.

When thrown on a hot plate, the substance decrepitates, and burns with a violet flame.

β-Bromo-α-triazoethane (Triazoethyl Bromide), $N_3 \cdot CH_2 \cdot CH_2Br$.

Although triazoethyl bromide has been obtained by the action of bromine on triazoethyl alcohol in presence of amorphous phosphorus, this is not the most convenient method of preparation, the interaction of phosphorus tribromide and the alcohol, when moderated by a diluent such as ether or petroleum, leading to more satisfactory results. One hundred grams of triazoethyl alcohol, covered with 100 c.c. of petroleum (b. p. 40°) in a flask surrounded with melting ice, were treated slowly with 112 grams of phosphorus tribromide in 250 c.c. of the same petroleum, the mixture being shaken vigorously after each portion was added; phosphorous acid separated, and a heavy, pale brown, viscous oil, insoluble in petroleum, constituted a large proportion of the product. After three hours on the water-bath under reflux, the less dense liquid was decanted, and the viscous residue shaken several times with small quantities of petroleum, which were added to the decanted solution of triazoethyl bromide; any excess of phosphorus tribromide

was destroyed by agitation with small quantities of water, and the liquid having been treated with ignited sodium sulphate, petroleum was boiled away, and the residue distilled under diminished pressure. The best yield obtained by this process was only 58 grams, representing about 34 per cent. of the amount anticipated:

0.0341 gave 15.9 c.c. N_2 at 24° and 765 mm. $N=28.00$.

0.4912 .. 0.6198 AgBr. $Br=53.38$.

$C_2H_4N_3Br$ requires $N=28.02$; $Br=53.33$ per cent.

Triazoethyl bromide is a colourless liquid, having the odour of ethylene dibromide, and rapidly becoming yellow when exposed to light: it boils at $49^\circ/20$ mm., and has the density $1.6675/19^\circ$. Action with concentrated sulphuric acid and with a solution of stannous chloride in hydrochloric acid resembles that of the chloro-compound, but hot alcoholic silver nitrate leads more readily to the elimination of halogen than in the case of that substance, and the above determination of bromine was carried out by this agent. The bromide does not become ignited when thrown on a hot plate, merely decrepitating mildly.

Attempts have been made to identify the viscous, brown oil which accompanies triazoethyl bromide when prepared by the foregoing method, so far without success. It is the production of this substance which is responsible for the disappointing yield, and is particularly inconvenient because triazoethyl bromide is the starting material for the chloride and the iodide. The presence of phosphorus, bromine, and the triazo-group suggested that the substance might be the bromide of bistriazoethylphosphorous acid, $(N_3CH_2CH_2O)_2PBr$, but the bromine content was much too low; it may be a mixture of this substance with triazoethyl phosphite, $(N_3CH_2CH_2O)_2P$, but an attempt to recover triazoethyl alcohol from it by hydrolysis was not successful.

3-Iodo- α -triazethane (Triazoethyl Iodide), $N_3\cdot CH_2\cdot CH_2I$.

The method employed for this preparation was the one recently described by Finkelstein (*Ber.*, 1910, **43**, 1523), and was found to be expeditious and economical. Fifty-eight grams of triazoethyl bromide were added to a solution of 60 grams of sodium iodide in 400 c.c. of dry acetone, sodium bromide being precipitated immediately; the mixture having remained at the ordinary temperature during the night, action was completed by heating under reflux, when about two-thirds of the solvent was distilled off, and the residue poured into water contained in a separating funnel, from which the heavy, dark brown liquid was then tapped. This was mixed with the ether used for extracting the triazoethyl iodide from the aqueous acetone, and shaken vigorously with a little mercury

in order to remove dissolved iodine, the residue from the dried ether being then distilled under diminished pressure, yielding 43 grams:

0.0814 gave 15.5 c.c. N_2 at 23° and 764 mm. $N = 21.58$.

0.4270 „ 0.5063 AgI. $I = 64.12$.

$C_2H_4N_3I$ requires $N = 21.32$; $I = 64.45$ per cent.

Triazoethyl iodide boils at $68^\circ/20$ mm., and when freshly distilled is colourless, but quickly becomes pale red; the odour resembles exactly that of ethyl iodide. It has the density $1.9154/25^\circ$, and is able to dissolve mercuric iodide, a property brought to light by the fact that a specimen which had been decolorised by agitation with mercury left a considerable residue of the salt on redistillation. The action with stannous chloride in hydrochloric acid is more brisk than in the case of the other triazoethyl halides, which the iodide resembles, however, in regard to interaction with concentrated sulphuric acid. Behaviour on the hot plate is similar to that of triazoethyl chloride.

It was hoped that a variety of interesting substances might be obtainable from typical compounds containing replaceable hydrogen by triazoethylation, but hitherto we have not been successful in this direction. *p*-Nitrophenol, for instance, when heated in dry benzene with silver oxide and triazoethyl iodide, gave a brown oil which did not invite further examination. *iso*Nitrosocamphor also gave an oil, remaining liquid during four months, and containing 22.35 per cent. of nitrogen ($C_{12}H_{18}O_2N_4$ requires $N = 22.4$ per cent.). Silver and lead cyanates were heated in ether and in benzene at the boiling points of these with triazoethyl iodide during many hours, but triazoethylcarbimide could not be recognised, although in absence of a diluent, some action takes place at about 100° , as indicated by a mild explosion which occurred. Silver cyanide developed the carbylamine odour when heated with triazoethyl iodide during two days on the water-bath, but the proportion of material remaining unchanged at the end of the experiment was too large to hold out any prospect of success. Bistriazoethyl sulphate appears to be formed when triazoethyl iodide is heated in dry benzene with silver sulphate, production of silver iodide being clearly indicated; the residue left by the solvent on evaporation did not distil at $140^\circ/1$ mm., but when hydrolysed with 30 per cent. potassium hydroxide, the liquid contained potassium sulphate, unmixed with iodide.

An attempt was made to prepare bistriazoethyl ether by heating 5 grams of triazoethyl alcohol and 11.3 grams of triazoethyl iodide with 15 grams of dry silver oxide on the water-bath during five days, but the entire product distilled at $85^\circ/35$ mm., weighed

5 grams, and contained 48.3 per cent. of nitrogen; this is the amount required by triazoethyl alcohol itself, whilst bistriazoethyl ether contains 53.8 per cent., from which it would appear that in the above experiment the triazoethyl alcohol remained unchanged, whilst the triazoethyl iodide was transformed into triazoethylene and diffused out of the apparatus.

β-Triazoethyl Ether, $N_3 \cdot CH_2 \cdot CH_2 \cdot O \cdot C_2H_5$.

Twenty grams of triazoethyl alcohol and 50 grams of ethyl iodide were allowed to remain in darkness with 50 grams of dry silver oxide during two days, being then heated on the water-bath with occasional addition of small quantities of ethyl iodide. After one week, the liquid was separated and distilled under diminished pressure:

0.1057 gave 33.5 c.c. N_2 at 21° and 763 mm. $N = 36.39$.

$C_4H_9ON_3$ requires $N = 36.51$ per cent.

The substance is a colourless liquid, boiling at $49^\circ/25$ mm., and having the density $0.9744/24^\circ$. The odour resembles that of chloro-ether, and in steam is pungent and sweet. With concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid, there is a vigorous effervescence, but hot concentrated alcoholic potassium hydroxide appears to be without action on triazoether, the azoimide nucleus remaining intact. Triazoethyl ether does not explode when thrown on a hot iron plate, the vapour burning with a luminous, white flame.

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CCCLXIV.—*The Intermolecular Condensation of Aromatic Sulphinic Acids. Part I.*

By THOMAS PERCY HILDITCH.

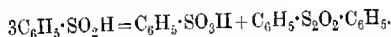
THE well-known tendency of aromatic sulphinic acids to enter into combination with other benzenoid residues through the elimination of water is more than maintained in the corresponding acid chlorides, which, as was observed when the latter compounds were originally obtained in a pure condition (Hilditch and Smiles, *Ber.*, 1908, 41, 4113), are exceedingly reactive and unstable. In the course of some work on the reduction of these chlorides, it was noticed that, if too much heat was applied during their preparation

or the subsequent treatment, decomposition set in, and white, crystalline, insoluble compounds, sometimes accompanied by tarry matter, were formed in considerable quantity.

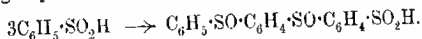
The present communication describes some experiments undertaken to elucidate the nature of these by-products. It was found that by heating benzenesulphinyl chloride, $\text{C}_6\text{H}_5\cdot\text{SOCl}$, or *p*-toluenesulphinyl chloride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SOCl}$, either alone at 100° or in boiling chloroform, or in presence of a slight excess of thionyl chloride beyond that needed for the preparation of the acid chlorides, a semi-solid, dark-coloured mass was obtained, from which the various compounds formed were separated by successive extraction with light petroleum, alcohol, and toluene. Furthermore, in order to avoid the formation of tarry decomposition products when heat was applied, the condensing action of cold concentrated sulphuric acid on these two chlorides was investigated, and analogous products were obtained, whilst, finally, it was established that the free sulphinic acid, when left for a sufficient length of time in solution in cold concentrated sulphuric acid, underwent a similar change, and from experiments with a number of aromatic sulphinic acids, it appeared that the course of the reaction was conditioned largely by the substituents present in the benzene nucleus.

From a general point of view, it would appear that besides simple oxidation to sulphonic acids there are the following possibilities to be considered in this decomposition of sulphinic acids:

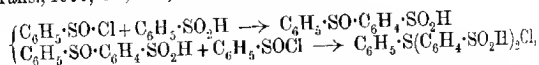
(i) The usual formation of disulphoxides, with possible further decomposition of the latter substances:



(ii) (a) Intermolecular condensation of the sulphinic acids, possibly involving more than two molecules of the acid, but not proceeding beyond the sulphoxide stage; for example:



(b) Further intermolecular condensation of the sulphoxides to complex sulphonium bases (compare Smiles and Le Rossignol, *Trans.*, 1906, **89**, 696; 1908, **93**, 745):



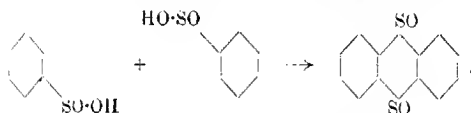
and so on.

As a matter of fact, definite evidence of the production of sulphonium derivatives has not been obtained, but both of the other reactions appear to take place, the one or the other predominating according to the manner of substitution in the sulphinic acid used. Thus, from the action of heat on benzene-

sulphonyl chloride, a quantity of diphenyl disulphide and the white, insoluble compound mentioned above was formed, whilst *p*-toluenesulphonyl chloride yielded under similar conditions a mixture of di-*p*-tolyl disulphoxide and a small amount of di-*p*-tolyl- α -disulphonc.

On the other hand, benzenesulphinic, *o*-toluenesulphinic, and α -naphthalenesulphinic acids reacted in the presence of concentrated sulphuric acid to form varying amounts of the insoluble products, together with disulphoxides. As much as 50 per cent. yields of the insoluble compound were obtained from benzenesulphinic acid, but only about 20 per cent. of the two other acids was converted to the corresponding insoluble derivative. Finally, *p*-toluenesulphinic, *p*-ethoxyphenylsulphinic, β -naphthalenesulphinic, and *o*-carboxybenzenesulphinic acids gave no "insoluble" product whatever, but usually furnished small amounts of disulphoxides.

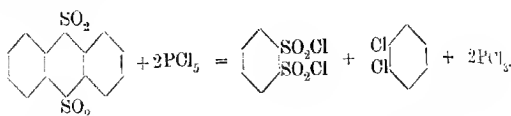
Of these various compounds, the white, insoluble substances, which in the first place attracted attention to this decomposition, are perhaps the most interesting. Since these were not α -disulphoncs, it appeared probable that they had been formed by means of the condensation (ii) (a) referred to above, but from their insolubility in sodium hydroxide solutions it did not seem likely that any free sulphinic acid group was present in their molecules. Accordingly, the possibility of the remaining sulphonyl radicle having entered into the reaction had to be considered, and at first sight it appeared that derivatives of diphenylene α -disulphide had been formed:



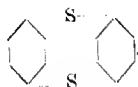
It soon became evident, however, from both physical and chemical properties of the products under investigation that they were not derived from ordinary diphenylene α -disulphide, and attention was next paid to a statement by Genvresse (*Bull. Soc. chim.*, 1896, [iii], 15, 421, 1038; 1898, [iii], 17, 599) that in the usual preparation of diphenylene α -disulphide large quantities of insoluble by-products were formed, and that under suitable conditions as much as 80 per cent. yields of an insoluble compound isomeric with diphenylene α -disulphide could be obtained from benzene, sulphur, and aluminium chloride. Genvresse suggested at the time that these compounds were para-condensation products, and that ordinary diphenylene disulphides contained meta-disulphide ring systems.

Recently, however, Deuss (*Ber.*, 1908, 41, 2329) has established the constitution of diphenylene disulphide as an ortho-ring system by heating diphenylene disulphone, $\text{C}_6\text{H}_4[\text{SO}_2]_2\text{C}_6\text{H}_4$, with phosphorus

pentachloride, when a mixture of *o*-dichlorobenzene and benzene-*o*-disulphonyl chloride was obtained according to the equation:



On treating the insoluble product derived from benzenesulphinic acid according to Deuss' directions, the author has obtained solid *p*-dichlorobenzene and benzene-*p*-disulphonyl chloride in sufficient amount for definite characterisation. It therefore appears that the compounds now being described are analogous to diphenylene *o*-disulphide, but are condensed into a ring system by means of their para-atoms:



A close comparison of the properties of these compounds with those described by Genvresse (*loc. cit.*) left no doubt that they were identical therewith; for example, the colour of their solutions in concentrated sulphuric acid is similar, but differs from that of the ortho-disulphides, whilst on oxidation a disulphone resulted identical in properties with that obtained by that author. Unfortunately, the compound from benzenesulphinic acid, which corresponds with a dioxide of Genvresse's isomeric compound, could not be reduced to the latter substance, owing probably to a simultaneous rupture of the ring system.

The proof of the orientation of these substances is strikingly supported by the fact that not a trace of the corresponding insoluble product could be obtained from either *p*-toluenesulphinic, *p*-ethoxyphenylsulphinic, or β -naphthalenesulphinic acids, the positions para to the sulphinyl group being occupied in these instances by other radicles.

The author has, however, not succeeded in deciding whether these products are really analogous to diphenylene *o*-disulphide or whether they consist of an indefinitely prolonged series of $\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot$ groups united in para-positions. The latter alternative might be thought possible in view of their insolubility in practically all organic solvents, of their high melting points, and of their not too well-defined crystalline structure, but, on the other hand, para-substituted compounds usually melt higher and are less soluble than the corresponding ortho-derivatives, and, again, their general stability and the substitution on oxidation of disulphones similar to diphenylene di-

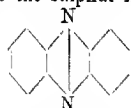
sulphone lend colour to the opinion that they are derived from the simple ring system:



A determination of molecular weight, which would have definitely established the point, was unfortunately quite out of the question, owing to the exceedingly slight solubility or volatility of any of the compounds.

There is, however, little reason to suppose that a para-ring system as depicted above would be less stable, although less familiar, than the usual six-membered ring, for since it is generally conceded that the para benzenoid atoms are almost as closely related in space as the ortho atoms, the above ring system will partake much more nearly of the nature of a six-membered than of the ten-membered heterocyclic chain which at first sight it appears to be.

Before describing the experimental part of this investigation, it will be well to discuss the mechanism of the condensations which take place in diphenylene disulphide syntheses, and especially the non-appearance from sulphinic acids of any ortho-ring products. Speaking in general terms, the numerous syntheses of heterocyclic ring systems which have been worked out do not permit of any choice of orientation on the part of the molecules concerned. Thus, in the case of phenazine, the nitrogen atoms in which are situated similarly to the sulphur in diphenylene disulphide, derivatives of

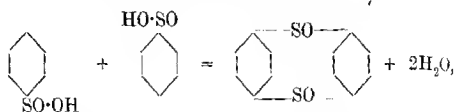
the system  result from o-phenylenediamine either

by oxidation in presence of phenols (Ris, *Ber.*, 1886, 19, 2207), or by condensation with catechol or derivatives of o-quinones (Hinsberg, *Annalen*, 1896, 292, 258), but the oxidation of aniline itself leads not to phenazine, but to the "aniline-black" dyes, in which a number of benzene nuclei are united by means of nitrogen atoms each in a para-position with respect to the next.

It seems probable that similar influences determine the course of ring formation from sulphinic acids and mercaptans; moreover, the preference for para condensation is emphasised in the case of sulphur compounds by the fact that, *ceteris paribus*, in the condensation of sulphinic acids or sulfoxides with phenolic ethers (Smiles and Le Rossignol, *loc. cit.*) para-substituted products predominate over ortho, the latter, indeed, being frequently not formed at all.

Again, all the synthetic methods for the preparation of di-

phenylene *o*-disulphides involve much loss of product owing to the formation of insoluble compounds, and it appears to the author that in most of these syntheses the formation of the disulphide is due to a secondary reaction, and may be ascribed to the fact that the starting materials are derivatives of phenyl mercaptan rather than of the more oxidised benzenesulphinic acid. The condensation of sulphinic acids is explained readily by the equation:



and it is probable that the underlying cause of all the earlier diphenylene disulphide syntheses is the production of temporary hydroxylic sulphur derivatives of the type $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{OH}$, rather than the simultaneous removal of a hydrogen atom from a mercaptan group and from a benzene nucleus by means of extraneous oxygen (compare Davis and Smiles, this vol., p. 1292).

Thus the chief methods extant for the synthesis of diphenylene *o*-disulphides are as follows:

(a) Action of sulphur on benzene in presence of aluminium chloride (Stenhouse, *Annalen*, 1869, **149**, 250; Krafft and Lyons, *Ber.*, 1896, **29**, 436).

(b) Action of aluminium chloride on mercaptans or disulphides (Deuss, *Rec. trav. chim.*, 1908, **27**, 145; 1909, **28**, 136).

(c) Action of hot concentrated sulphuric acid on mercaptans, disulphides, or disulphoxides (Fries and Volk, *Ber.*, 1909, **42**, 1170).

These reactions have been explained by the transitory formation of various oxidation and reduction products or by temporary isomerisation of the compounds involved, but it is evident that a simpler and more comprehensive explanation of the whole series results from the hypothesis that derivatives of sulphonylic acids are first produced, as has been assumed by Davis and Smiles (*loc. cit.*) in the formation of thioxanthenes, and by Hinsberg (*Ber.*, 1903, **36** 109) in the formation of hydroxydiphenyl sulphide from benzenesulphinic acid and phenol.

The process is thus similar to the condensation of the sulphinic acids, and differs only in that, whilst in the latter case no ortho-condensation occurs, in the former instance derivatives of diphenylene *o*-disulphide are formed in varying, but subsidiary, proportions.

It should be mentioned here that phenyl mercaptan itself, on being kept for some hours in concentrated sulphuric acid at the ordinary temperature, was converted to a mixture of a small amount

of diphenylene *o*-disulphide and about 70 or 80 per cent. of diphenylene *p*-disulphide.

The decomposition of disulphoxides in cold concentrated sulphuric acid is at present under investigation.

EXPERIMENTAL.

Action of Heat on Benzene- and p-Toluene-sulphinyl Chlorides.

(a) Five grams of benzenesulphinic acid were converted to the chloride by solution in ether and treatment with the theoretical quantity of thionyl chloride. It is found that this method yields a much cleaner product than the course formerly pursued of allowing excess of thionyl chloride to act on the undissolved acid in the cold. The ether was subsequently evaporated, and the residue heated on the water-bath for about an hour, when abundant evolution of hydrogen chloride took place. At the end of this period, the semi-solid product was extracted several times with boiling alcohol, after which the colourless, insoluble residue, which could not be crystallised from even such high boiling solvents as nitrobenzene or aniline, was dried at 130° and then analysed:

0.1023 gave 0.2186 CO_2 and 0.0321 H_2O . $\text{C} = 58.26$; $\text{H} = 3.49$.

$\text{C}_{12}\text{H}_5\text{O}_2\text{S}_2$ requires $\text{C} = 58.07$; $\text{H} = 3.23$ per cent.

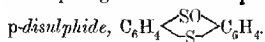
The alcoholic extract was found to contain a smaller quantity of diphenyl disulphide, melting at 59°, and identified with that substance by the mixed melting-point method.

(b) Two equal portions of benzenesulphinic acid were taken; one was converted into the acid chloride, and then heated with the other for some hours in boiling chloroform solution. As in the first instance, a large amount of diphenylene *p*-disulphide, together with a smaller amount of diphenyl disulphide, was obtained.

(c) Equal weights of benzenesulphinyl chloride and *p*-toluenesulphinic acid were heated in boiling chloroform for some time. After the evaporation of the chloroform, the product, which was very dark coloured, was first extracted with light petroleum, from which on evaporation a pale yellow oil was obtained, which was not closely examined, but appeared to be phenyl-*p*-tolyl disulphide (Otto and Rössing, *Ber.*, 1886, **19**, 3133). The residue was boiled with alcohol several times to remove tarry by-products, and an insoluble powder was thus formed, which again gave analytical numbers corresponding with diphenylene *p*-disulphoxide.

(d) Five grams of benzenesulphinic acid were heated for an hour with an amount of thionyl chloride in slight excess of that necessary for complete conversion to the acid chloride. The usual evolution of hydrogen chloride occurred, and the residue was extracted with

boiling light petroleum, which removed a small amount of diphenyl disulphide, and then with boiling toluene, from which there separated a quantity of a white, crystalline substance, melting and decomposing at 180°. This proved to be a *monoxide of diphenylene*,



0.1161 gave 0.2673 CO₂ and 0.0398 H₂O. C=62.77; H=3.80.

0.1192 „ 0.2712 CO₂ „ 0.0420 H₂O. C=62.04; H=3.91.

C₁₂H₈OS₂ requires C=62.07; H=3.45 per cent.

For comparison with this compound a sample of the monoxide of diphenylene *o*-disulphide was prepared from diphenylene *o*-disulphide by the method used by Fries and Volk (*loc. cit.*) in the preparation of the monoxide of ditolylene *o*-disulphide from ditolylene *o*-disulphide. Two grams of synthetic diphenylene *o*-disulphide, melting at 159°, were dissolved in glacial acetic acid, and dilute nitric acid (1:5) was added until a turbidity appeared. The solution was set aside for twenty-four hours at the ordinary temperature, and then poured into water. The precipitate was collected and crystallised from alcohol, when it formed colourless, glistening prisms, readily soluble in glacial acetic acid, benzene, or toluene, more sparingly so in alcohol, and melting at 148°:

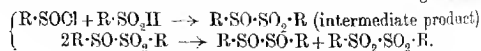
0.1160 gave 0.2607 CO₂ and 0.0369 H₂O. C=61.81; H=3.57.

C₁₂H₈OS₂ requires C=62.07; H=3.45 per cent.

(c) On similarly heating 5 grams of *p*-toluenesulphinyl chloride in boiling chloroform, much tarry matter was produced, and, after evaporation of the chloroform, extraction with light petroleum yielded a white, crystalline substance, which melted at 74–76°, and appeared from its other properties to be di-*p*-tolyl disulphoxide (Found, C=61.06; H=6.34. Calc., C=60.43; H=6.04 per cent.)

The residue was decolorised by repeated boiling with alcohol, and was found to crystallise from boiling toluene in small prisms, which melted at 210–212° (di-*p*-tolyl *α*-disulphone melts at 212°: Kohler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 219; 221°: Hilditch, *Trans.*, 1908, **93**, 1524). (Found, C=53.20; H=4.17; C=54.22; H=5.49. Calc., C=54.20; H=4.52 per cent.)

No trace of diphenylene *p*-disulphide derivatives was observed, and it would appear that, the para-position being already occupied by a methyl group, the reaction had taken the alternative course (i) referred to on p. 2580, in the presence of a certain amount of free sulphinic acid which must be assumed to have been regenerated:



Action of Cold Concentrated Sulphuric Acid on Benzenesulphinic Acid.

(a) Two grams of benzenesulphinic acid were converted to the chloride and poured into cold concentrated sulphuric acid. Hydrogen chloride was immediately disengaged in abundance throughout the solution in the form of minute bubbles, and after half an hour at the ordinary temperature, the reaction mixture was poured on crushed ice. The solid product was separated and boiled with alcohol, thus removing a small amount of diphenyl disulphoxide, which melted at 45° . The residuc (diphenylene *p*-disulphoxide) was dried at 130° and analysed. (Found, C=58.22; H=3.35. Calc., C=58.07; H=3.23 per cent.)

(b) Ten grams of benzenesulphinic acid were left in solution in excess of cold concentrated sulphuric acid. The mixture, which was at first colourless, gradually turned purple, and was eventually of an almost black hue. On pouring into a large bulk of cold water, the colour entirely disappeared, and a granular, cream-coloured, solid product separated, and was collected and dried on a porous tile.

The whole was then boiled with alcohol under reflux for a time and again filtered; from the alcoholic filtrates about half a gram of diphenyl disulphoxide was obtained, which crystallised from light petroleum in characteristic, wax-like crystals, melting at 46° . (Found, C=57.00; H=4.20. Calc., C=57.60; H=4.00 per cent.)

The insoluble part of the product, when boiled for some time with alcohol, lost its crystalline appearance, and swelled up to a viscid, indiarubber-like mass. After removing the alcohol, however, the substance quickly became brittle again, and appeared gradually to break up into a microcrystalline powder on long keeping. This behaviour was also noticed with all the previously-described preparations of diphenylene *p*-disulphoxide, and also with the substituted derivatives subsequently mentioned.

The substance, which was then almost pure, was further submitted to two different methods of purification.

(i) A portion was boiled with toluene under reflux for some time, and was then collected and dried at 130° for some hours to remove adsorbed solvent and moisture, which was otherwise retained remarkably firmly. Diphenylene *p*-disulphoxide, as thus prepared, is a cream-coloured powder, practically insoluble in all the organic solvents tried (even in boiling nitrobenzene or aniline), but dissolving with a greenish-black colour in concentrated sulphuric acid. It commenced to soften and decompose without actually melting at 305° :

0.1035 gave 0.2194 CO_2 and 0.0298 H_2O . $\text{C}=57.81$; $\text{H}=3.17$.

$\text{C}_{12}\text{H}_8\text{O}_2\text{S}_2$ requires $\text{C}=58.07$; $\text{H}=3.23$ per cent.

(ii) The remainder of the preparation was boiled with water for two hours, and then collected and dried at 130° as above:

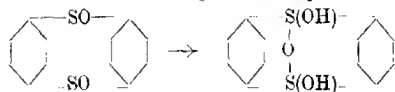
0.1353 gave 0.2685 CO_2 and 0.0485 H_2O . $\text{C}=54.12$; $\text{H}=3.98$.

0.1292 „ 0.2540 CO_2 „ 0.0401 H_2O . $\text{C}=53.60$; $\text{H}=3.45$.

$\text{C}_{10}\text{H}_8\text{O}_2\text{S}_2 \cdot \text{H}_2\text{O}$ requires $\text{C}=54.13$; $\text{H}=3.76$ per cent.

An attempt was made to remove this molecule of water by prolonged boiling with xylene, but a subsequent analysis showed that the composition of the product had not been altered. (Found. $\text{C}=53.34$; $\text{H}=3.53$.)

Water thus firmly attached is inconsistent with the presence of water of crystallisation, and it can only be surmised that some such hydrate formation as the following had taken place:



Oxidation of Diphenylene p-Disulphoxide.

Two grams of diphenylene *p*-disulphoxide were boiled for eight hours with a slight excess of anhydrous chromic acid in glacial acetic acid; oxidation ensued, and the hot reaction mixture was filtered, and the residue washed with boiling water until all traces of green chromium salts were removed, and then with boiling alcohol; an amorphous, white powder, which neither melted nor changed in appearance below 350° , was left. A sample dried in a vacuum desiccator was analysed:

0.0994 gave 0.1693 CO_2 and 0.0362 H_2O . $\text{C}=46.45$; $\text{H}=4.05$.

0.1380 „ 0.2343 CO_2 „ 0.0422 H_2O . $\text{C}=46.30$; $\text{H}=3.40$.

$\text{C}_{12}\text{H}_8\text{O}_4\text{S}_2 \cdot 2\text{H}_2\text{O}$ requires $\text{C}=45.57$; $\text{H}=3.80$ per cent.

Reduction of Diphenylene p-Disulphoxide.

(a) Two grams of hydrated dioxide were heated for eight hours with 5 grams of sulphur at 150° ; this process reduces the ortho-disulphoxide to the corresponding disulphide (Krafft and Lyons, *loc. cit.*), but on removal of excess of sulphur by means of carbon disulphide, the para-disulphoxide was found to have been unattacked.

(b) Three grams of the dioxide were heated under pressure at 160 – 180° with 1 gram of red phosphorus and 10 c.c. of hydriodic acid (D 1.7). Considerable pressure was generated, and the product was poured into water and extracted with benzene. A large pro-

portion of insoluble matter was removed by filtration of the whole of the liquid, and the benzene layer was then dried and evaporated. It yielded a small amount of an oil, which soon crystallised, and, when purified by light petroleum, melted at 61° ; analysis confirmed the supposition that this was diphenyl disulphide. (Found, $C=66.01$; $H=5.01$. Calc., $C=66.06$; $H=4.60$ per cent.)

An attempt made to purify the insoluble product, which was assumed to be diphenylene *p*-disulphide, by sublimation, led to the evolution of iodine vapours, and further experiments showed that the substance contained chemically bound iodine in quantity. Analysis proved that one atom of iodine was present in each diphenylene *p*-disulphide residue, but as the compound was not the desired parent substance it was not further studied; it is probably either an iododiphenylene *p*-disulphide or else a compound of the type $H_2S \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot I$, formed by rupture of the para-ring system:

0.1800 gave 0.2750 CO_2 and 0.0516 H_2O . $C=41.68$; $H=3.18$.

$C_{12}H_7S_2I$ requires $C=42.11$; $H=2.05$ per cent.

$C_{12}H_9S_2I$ „ $C=41.86$; $H=2.62$ „

Proof of the Constitution of Diphenylene p-Disulphoxide.

Six grams of the disulphoxide were ground in a mortar with 30 grams of phosphorus pentachloride, and heated in sealed tubes at 220° for six hours. The contents of the tubes were poured on ice, and subsequently extracted with ether; this extract was dried, the ether evaporated, and the residue distilled in a current of steam. The aqueous distillate contained an oil which quickly solidified to a mass of white needles, melting at 53° , and possessing the characteristic odour of *p*-dichlorobenzene. (Found, $C=48.60$; $H=2.25$. Calc., $C=48.98$; $H=2.71$ per cent.)

Since both *o*- and *m*-dichlorobenzene are liquids, the identity of the product was considered to be satisfactorily established.

The non-volatile portion of the product was extracted with ether and shaken with dilute sodium hydroxide; on evaporation of the dried ethereal solution, wax-like and not very well-defined crystals separated, melting at 131 – 133° ; benzene-*o*-disulphonyl chloride melts at 105° ; the *m*-compound at 63° ; and the *p*-compound at 132° . (Found, $C=26.70$; $H=1.26$. Calc., $C=26.18$; $H=1.46$ per cent.)

The compound was further characterised by conversion into the sparingly soluble diamide, which formed small, hard prisms, and melted at 295° . The ortho-compound melts at 233° , the meta at 227° , and the para at 288° . (Found, $C=29.92$; $H=3.89$. Calc., $C=30.51$; $H=3.39$ per cent.)

Condensation of Phenyl Mercaptan in Cold Concentrated Sulphuric Acid.

Five grams of phenyl mercaptan were dissolved in concentrated sulphuric acid at the ordinary temperature, and the mixture vigorously shaken to dissolve the crystalline cake of diphenyl disulphide, which rapidly formed. After twenty-four hours, the deep purple-black reaction mixture was poured into a large bulk of cold water, the precipitate collected, dried, and extracted successively with boiling light petroleum and with hot alcohol. The absence of any solid on evaporation of the former solvent proved that no disulphide was left unattacked, whilst from the alcoholic filtrates a quantity of colourless, crystalline material was recovered, which, after further purification from alcohol, melted at $156-159^{\circ}$. A sample mixed with some pure diphenylene *o*-disulphide possessed the same melting point. About a gram of diphenylene *o*-disulphide, dissolving in concentrated sulphuric acid to a characteristic deep purple solution, was thus obtained. (Found, $C=66.66$; $H=4.54$. Calc., $C=66.67$; $H=3.70$ per cent.)

About 3 grams of a cream coloured, amorphous powder, insoluble in boiling alcohol, were left from the above extraction, and this was boiled with acetic acid for an hour, collected, and dried at 130° . (Found, $C=67.04$; $H=3.88$. Calc., $C=66.67$; $H=3.70$ per cent.)

Genvresse (*loc. cit.*) states that diphenylene *p*-disulphide can be purified by sublimation; the sample under consideration was submitted to purification by this means, but did not sublime sufficiently readily for any quantity of the purified substance to be so isolated; enough was obtained, however, in minute, white needles for a determination of the melting point; the compound melted and decomposed at $290-295^{\circ}$ (295° , Genvresse). Its solution in concentrated sulphuric acid was of a greenish-black hue.

Condensation of Other Aromatic Sulphinic Acids in Cold Concentrated Sulphuric Acid.

(a) *p*-Toluenesulphinic Acid.—The sulphinyl chloride, on solution in sulphuric acid, evolved hydrogen chloride copiously, and gave a greenish-brown solution, which ultimately became deep purple. On pouring into cold water, no *p*-disulphide compound was obtained, and only a very small amount of disulphoxide, which melted at 76° .

A similar result was obtained from the condensation of the free acid.

(b) *p*-Phenetolesulphinic Acid.—The acid was dissolved in sulphuric acid in the usual manner, and the purple reaction mixture poured into water after a considerable time. The only insoluble

product was a quantity of di-*p*-phenetole disulphoxide, which melted at 139° (a sample of the disulphoxide prepared in the usual way from *p*-phenetolesulphinic acid melted at the same temperature).

(c) *β-Naphthalenesulphinic Acid*.—The condensation was conducted as usual; the products of the reaction were all soluble in cold dilute acid, the solution being very deeply coloured. Neither derivatives of a *p*-disulphide nor any disulphoxide could be detected.

(d) *α-Toluenesulphinic Acid*.—On separation of the products of condensation in sulphuric acid of 5 grams of *o*-toluenesulphinic acid, it was found that rather more disulphoxide derivative had been produced than in the other cases. The di-*o*-tolyl disulphoxide crystallised from acetone in short, colourless prisms, melting at $97-98^{\circ}$. (Found, C=60.09; H=5.06. Calc., C=60.45; H=5.04 per cent.)

On the other hand, only about 20 per cent. of the sulphinic acid was converted into *p*-disulphide derivative in this instance; the *dinaphthylene p-disulphoxide* was a soft, colourless, insoluble powder, which softened, without actually melting, at 280° :

0.0309 gave 0.2004 CO_2 and 0.0375 H_2O . C=60.12; H=4.58.

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}_2$ requires C=60.87; H=4.35 per cent.

(e) *α-Naphthalenesulphinic Acid*.—The amount of di-*α*-naphthyl disulphoxide obtained from the condensation was very small; it melted at 104° . A tolerably large proportion of insoluble matter resulted, but was contaminated by the presence of traces of dark-coloured products, even after prolonged boiling with various solvents. The probably still somewhat impure *dinaphthylene p-disulphoxide* finally analysed softened at $275-280^{\circ}$, and commenced to char at a rather higher temperature:

0.1902 gave 0.4760 CO_2 and 0.0730 H_2O . C=68.26; H=4.26.

$\text{C}_{20}\text{H}_{12}\text{O}_2\text{S}_2$ requires C=68.98; H=3.45 per cent.

(f) *o-Carboxybenzenesulphinic Acid*.—A sample of this acid was also submitted to the condensation in concentrated sulphuric acid. The dried product of the reaction was completely soluble in hot alcohol, no *p*-disulphide compounds having therefore been produced. From the alcoholic solution, pale yellow crystals of *di-o-carboxyphenyl disulphoxide*, melting at 228° , separated; the total amount of this product corresponded with about 10 per cent. of the original sulphinic acid employed:

0.1546 gave 0.2808 CO_2 and 0.0444 H_2O . C=49.52; H=3.20.

$\text{C}_{14}\text{H}_{10}\text{O}_6\text{S}_2$ requires C=49.71; H=2.96 per cent.

CCLXV.—4- β -Aminoethylglyoxaline (β -Iminazolyethylamine) and the other Active Principles of Ergot.*

By GEORGE BARGER and HENRY HALLETT DALE.

For many years ergot has been notorious among drugs on account of the ignorance and division of opinion concerning the nature of its active principles. The problem had, indeed, approached solution in 1875, with Tanret's discovery of ergotinine and Buchheim's suggestion that ergot owes its activity to decomposition products of proteins produced by putrefaction. This discovery and suggestion were largely obscured by the work of subsequent investigators, who resulted rather in the physiological characterisation of impure products (sphacelinic acid, sphacelotoxin, etc.) than in chemical isolation of active principles.

Of late years, however, a considerable measure of agreement has been reached. The alkaloid ergotoxine (Barger and Carr) was also found by Kraft, who named it hydroergotinine, and the formulae assigned to ergotinine and ergotoxine (Trans., 1907, 91, 337) have been confirmed by Tanret and by Kraft respectively. There is also a consensus of opinion regarding the effect of ergotoxine on the blood-vessels and uterus, and its activity in producing gangrene.

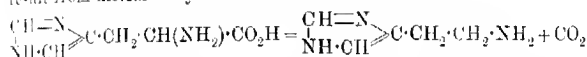
Thus ergot, in common with many drugs, contains a complex physiologically active alkaloid. In addition, however, there are present in ergot a number of simpler bases, derived from amino-acids by the elimination of carbon dioxide. Such bases are generally formed in putrefaction. Ergot, as a fungus, is more closely related to bacteria than to the higher plants, from which all other important vegetable drugs are derived. Thus the peculiar nature of these active principles of ergot is due to its peculiar systematic position in the vegetable kingdom.

Putrefaction bases were first isolated from ergot by Rieländer (*Sitzungsber. Ges. Naturw. Marburg*, August 5th, 1908), who found putrescine and cadaverine, which only have a feeble physiological action. The first markedly active base of this class, *p*-hydroxy-phenylethylamine, was isolated from ergot by ourselves (Barger and Dale, *Proc. Physiol. Soc.*, May 15th, 1909, in *J. Physiol.*, 1909, 38, lxxvii; Barger, Trans., 1909, 95, 1123). It is formed from tyrosine during putrefaction, but appears to be present also in fresh ergot. It is the chief pressor constituent of most aqueous ergot extracts, but does not produce contraction of the isolated uterus of the non-pregnant cat. In addition, we showed that it

* A preliminary note on this subject was read at the meeting of May 26th, 1910.

anylamine (from leucine) is probably present in ergot, but in such proportion that it makes no significant contribution to the physiological action.

After the isolation of *p*-hydroxyphenylethylamine, there still remained unaccounted for the powerful action of certain aqueous ergot extracts in producing contraction of the isolated uterus, even of the non-pregnant cat, as observed by Kehrer. Since it was found quite impossible to remove the active substance from aqueous solution by means of organic solvents, a precipitation method had to be employed, and the ergot extract was subjected to the process worked out by Kutscher for the isolation of bases from meat extract. In this way we obtained a minute quantity of a crystalline picrate which gave Pauly's reaction with *p*-diazobenzenesulphonic acid, and exhibited in an intense degree the physiological action in question. It was not histidine picrate, for histidine was found to be inert; we therefore supposed it to be the picrate of 4- β -aminoethylglyoxaline (β -iminazolyethylamine), the base which would result from histidine by the loss of carbon dioxide:



and we confirmed this supposition by chemical and physiological comparison with a specimen of 4- β -aminoethylglyoxaline, very kindly sent us at our request by Dr. D. Ackermann, who a short time before had obtained this base by the putrefaction of histidine (*Zeitsch. physiol. Chem.*, 1910, **65**, 504). Simultaneously with ourselves, Kutscher (*Zentr. Physiol.*, 1910, **24**, 163) obtained a very active base from ergot, which he considered to be closely related to 4- β -aminoethylglyoxaline, although not identical with it, on account of a supposed difference in the physiological action of the two bases. It has, however, recently been shown that the differences in physiological action observed by Kutscher were presumably due to differences in the animals employed. One and the same base, whether from ergot or from histidine, can be made to produce the different effects described by Kutscher. On the other hand, the base from ergot and that from histidine, when tested successively on the same animal, gave identical effects. We have also analysed the picrate of the base from ergot, and have compared it and the picrolonate with the corresponding salts of 4- β -aminoethylglyoxaline (from histidine). As a result, we maintain our original conclusion (*Proc.*, 1910, **26**, 128) that, contrary to Kutscher's view, the base in question is identical with 4- β -aminoethylglyoxaline. It is therefore the second active principle of ergot belonging to the class of putrefaction bases derived from amino-acids. Its physiological activity is very great. A marked contraction of the isolated uterus

is produced by adding to the bath sufficient of the base to give a concentration of one part in 25 million parts of Ringer's solution: the effect of one part in 250 millions is often quite definite.

A third active principle of this class was quite recently found in ergot by Engeland and Kutscher (*Zentr. Physiol.*, 1910, **24**, 479). This is agmatine, $\text{NH}_3\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, discovered in herring roe by Kossel (*Zeitsch. physiol. Chem.*, 1910, **66**, 257). Its relation to arginine is analogous to that of 4- β aminoethylglyoxaline to histidine, and it is said to have a similar action on the uterus.

EXPERIMENTAL.

Among the ergot preparations examined by Kehrer, the *ergotinum dialysatum* of Wernich is one of the most potent. We soon found, in making this extract on a small scale, that the activity of the substance which passed through the dialysing membrane finally exceeded that of the original extract, suggesting that more of the active principle was being formed by an enzyme or by bacteria. The active principle is, however, also present in perfectly fresh ergot, for the physiological effect was produced by a sample of ergot grown by ourselves and tested within half an hour of plucking. The effect was also produced to a smaller extent by commercial extracts of meat and of yeast, and this observation led to the adoption of Kutscher's method for the isolation of bases from meat extract. To 500 c.c. of commercial dialysed ergot extract, 500 c.c. of a 20 per cent. tannin solution were added, which quantity just ensured complete precipitation; next day the clear, supernatant liquid was decanted, and freed from tannin by the addition of barium hydroxide; after filtration, the excess of barium hydroxide was removed by dilute sulphuric acid, and the excess of sulphuric acid, together with the last traces of tannin, were precipitated by adding a suspension of freshly prepared lead hydroxide. After filtration, the liquid was concentrated to 300 c.c., and acidified with phosphoric acid. After adding excess of silver nitrate (400 c.c. of a 20 per cent. solution) and filtering, we found that the whole of the active substance was in the filtrate. To the latter, 150 c.c. more silver nitrate were added, when a drop of the solution at once produced a brown precipitate of silver oxide on mixing with barium hydroxide. The whole of the solution was then precipitated with barium hydroxide, until a sample, on filtration, gave only a slight opalescence with ammoniacal silver nitrate. This precipitate (silver II of Kutscher's method) in one preliminary experiment contained nearly the whole of the active substance, but afterwards it was found convenient to add at once to the filtrate from the first silver precipitate enough barium hydroxide for complete precipitation.

was collecting together silver precipitates II and III of Kutscher.

After washing, the silver precipitate was carefully suspended in very dilute sulphuric acid, and decomposed by hydrogen sulphide. The filtrate from the silver sulphide was freed from hydrogen sulphide, neutralised, and evaporated to dryness. The residue was extracted several times with hot ethyl alcohol, in which the active principle was found to be sparingly soluble; a large quantity of inert matter was left behind. The residue remaining on evaporating the alcoholic solution was dissolved in a little water, and a hot saturated aqueous solution of picric acid was added. After keeping for some days, a brown, imperfectly crystalline picrate was collected, washed, and recrystallised from water. This picrate was converted into a solution of the hydrochloride, which was very active physiologically, and gave an intense red coloration with sodium *p*-diazobenzene-sulphonate (Pauly's reaction), suggesting a relationship to histidine. We had previously detected some activity in the crude histidine mother liquors obtained by hydrolysis of hemoglobin with hydrochloric acid; histidine itself was found to be inactive, but it became so to a slight extent on heating to 300°. We were thus led to suppose that the picrate we had isolated was that of 4- β -aminoethylglyoxaline. After two crystallisations from water, the picrate from ergot formed dark yellow, rhombic plates, melting and decomposing at 234–235°. A specimen of the picrate sent us by Dr. D. Ackermann, when heated simultaneously in a tube attached to the same thermometer, also melted at 234–235°, and when recrystallised by evaporation of the solution in a desiccator, yielded rhombic plates exactly similar to those of the ergot base. Windaus and Vogt (*Ber.*, 1907, 40, 3695) give the melting point as 239° on rapid heating, and the same crystalline form for a synthetic specimen of 4- β -aminoethylglyoxaline dipicrate. For analysis, the picrate was dried at 100° until constant:

0.0590 gave 0.0776 CO₂ and 0.0192 H₂O. C=35.8; H=3.6.

C₁₄H₁₂N₂(C₆H₃O₇N₃)₂ requires C=35.8; H=2.6 per cent.

We also prepared the very sparingly soluble picrolonate of the ergot base; it decomposed at 261° (Windaus and Vogt give 266° for 4- β -aminoethylglyoxaline dipicrolonate).

As the physiological action of the ergot base is also the same as that of 4- β -aminoethylglyoxaline, there is no room for doubt that the two bases are identical.

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CCLXVI.—*Viscosity and Association. Part I. Association of the Phenols.*

By FERDINAND BERNARD THOLE.

A STUDY of the literature on the subject of viscometry shows the existence of much evidence which indicates that association is accompanied by a considerable augmentation of viscosity (compare Dunstan and Thole, *Trans.*, 1909, **95**, 1556).

On the other hand, in a paper published by Jones and Venzey (*Amer. Chem. J.*, 1907, **37**, 405), it was suggested that the depression of the degree of association of a liquid is accompanied by an increase in its viscosity. The increase in viscosity produced when alcohols are dissolved in water was explained by these authors as being due to a diminution of the association of each component, resulting in an increase in the number of non-associated molecules, and therefore of the available frictional surface. From a study of the viscosity-concentration curves for aqueous solutions of many inorganic salts, they also concluded that ions of large atomic volume, such as potassium, rubidium, and cesium, give rise to the phenomenon of negative viscosity.

Since the relative degree of association of many phenols and their derivatives has been investigated by using a variety of physical methods, particularly cryoscopy, specific inductivity, and capillarity, it was considered of interest to compare the results obtained by viscometric methods with those determined by other physical methods.

Pinette (*Annalen*, 1888, **243**, 32) showed that the boiling points of the phenols are, in general, higher than those of their methyl ethers, and that ortho-substituted phenols boil at a lower temperature than their meta- and para-isomerides. The current ideas concerning association and steric hindrance are in accordance with these results, assuming the boiling points of similarly constituted compounds to vary in the same sense as the molecular weights.

Aston and Ramsay (*Trans.*, 1894, **65**, 168), by measurement of the molecular surface energy of phenol, concluded that it was considerably associated.

Auwers (*Ber.*, 1895, **28**, 2878) carried out a very comprehensive series of cryoscopic investigations of the molecular weights of various phenols in naphthalene solution. He showed that whilst phenol is considerably associated, ortho-substituted phenols are practically unassociated, the association increasing to a maximum with the para-compounds. Meta-substituted phenols are associated to an inter-

to some degree, but approximate more nearly to the para-series. In the ortho-series, the aldehyde group has the greatest effect in inhibiting association; then, in order, follow the carbethoxyl, nitro-, halogen, and finally alkyl groups.

Speranski (*Zeitsch. physikal. Chem.*, 1903, **46**, 70) determined the vapour pressures of solid solutions of β -naphthol in naphthalene, and concluded that the former compound is associated.

Philip and Haynes (*Trans.*, 1905, **87**, 998) measured the dielectric constants of phenol, its methyl and ethyl ethers, and of the cresols in benzene and in *m*-xylene solutions. Their results indicate that, whilst the ethers are unassociated, phenol and the cresols are distinctly associated, *o*-cresol to the least extent.

Hewitt and Winmill (*Trans.*, 1907, **91**, 441), using the capillarity method of Ramsay and Shields, studied the association of a considerable number of substituted phenols and allied substances. Their results are included in table I, and show that the phenols in general are associated, the association being least in the ortho-series. Considerable depression of association is produced by the carbethoxyl, nitro-, and halogen groups, but alkyl groups only exert a slight influence. Benzyl alcohol was shown to be associated, but the introduction of phenyl groups inhibits this to such an extent that benzhydrol and triphenylcarbinol are practically unassociated. It appears uncertain whether substitution in the meta- or para-positions has the greater effect, the results on this point being indecisive. It seems to the author, however, that, although the capillarity method will show satisfactorily whether or no a substance is associated, little trust can be placed in figures indicating the actual degree of association, for in a mixture one is not entitled to assume that the constitution of the surface layer is typical of that of the bulk of the liquid, and associated liquids may fairly be regarded as mixtures of molecular aggregates and simple molecules.

EXPERIMENTAL.

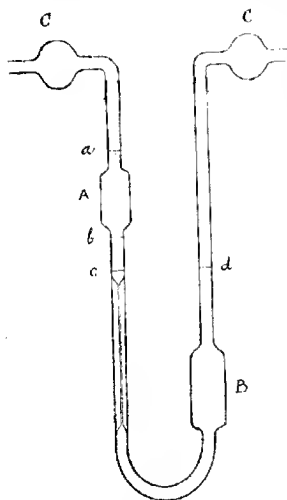
As the apparatus used has been considerably modified with a view to increased accuracy since it was previously described by the author (*this vol.*, p. 1251), a somewhat detailed account of the viscometer and the accompanying fittings may be of interest.

The viscometer was of the original Ostwald type, but was provided with four etched marks instead of two. Guard tubes were also attached to the two limbs, and were provided with bulbs, which contained cotton wool moistened with the liquid under investigation. By adopting this precaution, volatile liquids, such as acetone and benzene, may be safely used as solvents. The dimensions of the viscometer may, of course, be varied, according to the quantity and

nature of the liquid used. For the present research, the bulbs *A* and *B* contained approximately 3 and 5 c.c. of liquid respectively. The length of the capillary was 8 cm., and the diameter 0.025 cm.

Before use the viscometer was cleaned successively with hot chromic acid mixture, hot absolute alcohol, and boiling, filtered conductivity water. Finally, it was dried in a current of warm dust-free air. Every precaution is necessary to avoid the introduction of dust, as this will inevitably choke the capillary.

The clean, dry viscometer was suspended by means of a carrier provided with spring clips in a copper thermostat fitted with large



windows front and back. In this bath were fixed a stirrer connected with a small hot air motor, a standard thermometer, a Beckmann thermometer graduated to 0.01° , and a Lowry thermoregulator of the "spiral" pattern. The determinations were carried out in a laboratory allocated for the purpose, and the variation of temperature of the thermostat did not exceed 0.02° .

The liquid was filtered or, whenever possible, distilled into the viscometer, and after the apparatus had remained in the thermostat for ten minutes, the level of the liquid was adjusted to the marks *c* and *d*. Cotton wool contained in the guard

tubes *cc* was moistened with the liquid, the tubes attached, the viscometer accurately adjusted to a vertical position by means of three plumb lines, and the time of flow of the liquid from *a* to *b* measured in the usual way. A stop watch, reading to 0.2 second, was used. Usually about seven observations, differing by not more than 0.5 second, were made, and the mean was taken.

The densities were determined in a Sprengel pyknometer of 5 c.c. capacity, and in the case of phenol and *p*-chlorophenol in a 10 c.c. specific gravity bottle. Each estimation was repeated until concordant results were obtained, and a correction was introduced for the weight of displaced air.

The constants of the instruments were determined from time to

time, using conductivity water. The values adopted for the viscosity of water were those determined by Thorpe and Rodger.

For the two determinations at 130°, the ordinary thermostat was replaced by a large beaker filled with heavy petroleum and heated by a small burner. The temperature was regulated by hand, the maximum fluctuation being 0.2°.

The substances used in the research were carefully purified by repeated fractionation with a rod-and-disk column or by recrystallisation. In no case did the liquid used for the determination boil over a greater range than 0.2°. Unless otherwise stated, the reaction used boiled constantly. The source and method of purification of the materials is indicated below.

Phenol.—Kahlbaum's "synthetic" phenol. Fractionated three times.

Anisole.—The specimen used was obtained from a large quantity of the carefully dried ether.

Phenetole.—Purified in the same way as anisole.

Phenyl Acetate.—Prepared from synthetic phenol and acetic anhydride. The specimen was free from phenol and acetic acid.

Cresols.—Schuchardt's purest products, fractionated three times.

Tolyl Methyl Ethers.—Carefully dried and fractionated.

o-Chlorophenol.—Fractionated three times from a specimen supplied by Kahlbaum.

m-Chlorophenol.—Purified by freezing out and subsequent fractionation. The specimen boiled within 0.2°.

p-Chlorophenol.—Purified by freezing out and subsequent fractionation.

o-Nitrophenol.—Three times distilled in a current of steam, and finally recrystallised from absolute methyl alcohol.

m-Nitrophenol.—Twice recrystallised from pure benzene, and dried in a vacuum over paraffin wax.

p-Nitrophenol.—Freed from traces of the ortho-isomeride by means of a current of steam, twice recrystallised from dilute hydrochloric acid, and dried in a vacuum over potassium hydroxide.

Ethyl Salicylate.—Fractionated three times from a quantity of the pure ester.

Ethyl m-Hydroxybenzoate.—Twice recrystallised from pure benzene, and dried in a vacuum over paraffin wax.

Ethyl p-Hydroxybenzoate.—Twice recrystallised from absolute alcohol.

Salicylaldehyde.—Fractionated twice.

Benzyl Alcohol.—Prepared from re-distilled benzaldehyde by the Cannizzaro reaction, and fractionated three times. The specimen boiled within 0.2°.

Benzyl Acetate.—Fractionated three times.

Benzyl Methyl Ether.—Prepared from pure benzyl chloride and methyl-alcoholic sodium methoxide. The specimen was free from halogen and from methyl alcohol.

Benzhydrol.—Prepared from re-distilled benzaldehyde and magnesium phenyl bromide, and crystallised several times from light petroleum.

Triphenylcarbinol.—Recrystallised from benzene.

α - and β -Naphthols.—Fractionated from Schuchardt's purest products.

Amyl Acetate.—A large quantity of Kahlbaum's purest product was twice fractionated. It boiled within 0.5° .

Ethyl Alcohol.—Kahlbaum's absolute alcohol was fractionally distilled over cleaned calcium turnings.

As the differences of viscosity are most marked in the case of the pure substances, the viscosities of all those which are liquid at 45° were measured at this temperature. Since some of the compounds it was desirable to investigate are solid at this temperature, solutions of these substances had to be used.

Some care had to be exercised in the choice of a solvent which would have the least dissociating effect and at the same time would readily dissolve the substances, which would have a low vapour tension (to minimise errors due to evaporation), and could easily be obtained in a fairly pure state. Amyl acetate was finally chosen as fulfilling these conditions most nearly.

The solutions used were of equimolecular strength, $1/100$ th of a gram-molecular weight of the substance being accurately weighed into a stoppered weighing bottle, and dissolved in 6 c.c. of amyl acetate, which was run in from a suitably graduated pipette.

In two instances (with ethyl *p*-hydroxybenzoate and triphenylcarbinol), it was found impossible to prepare solutions of this strength, and in these cases the viscosities of several solutions of lower concentration were determined, the value for the stronger solution being obtained by extrapolation. Although the accuracy of these results may not be of the same order as in the direct determinations, the qualitative nature of the results is not affected.

It has been shown (Dunstan and Wilson, *Trans.*, 1907, **91**, 38; Getman, *Amer. Chem. J.*, 1903, **30**, 1077) that the value of the

expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ indicates to some extent the existence of

association in a liquid. For each particular series of compounds this quantity is approximately constant, and for non-associated liquids does not exceed 60. The values for hydroxylated liquids are, however, much higher, those for water, ethyl alcohol, and ethylene

glycol being respectively 494, 193, and 2750, and the variation of the value of this expression is a very sensitive indication of association.

The values for each of the substances investigated is given in the tables, and affords, perhaps, the best means of comparing the results. It should be noted, however, that this value is affected to some extent by symmetry as well as by association. This is seen in the case of the tolyl methyl ethers, and more particularly in the case of benzyl methyl ether, where the value of $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ is slightly higher than the mean figure for the unassociated ethers, probably owing to the comparatively long side-chain.

TABLE I.
The Pure Substances at 45°.

| Substance. | Time of flow in seconds. | Density. | Viscosity. | η Mol. vol. $\times 10^6$ | Hewitt and Winmill's association constants. |
|------------------------------------|-----------------------------|----------|------------|-----------------------------------|---|
| Phenol | 837.2 | 1.055 | 0.01036 | 453.0 | 1.3 |
| Phenyl acetate | 374.2 | 1.052 | 0.01799 | 136.0 | — |
| Anisole | 167.0 | 0.9707 | 0.007409 | 66.6 | — |
| Phenetole | 191.4 | 0.9427 | 0.008249 | 63.8 | — |
| <i>p</i> -Chlorophenol | 1044.8 | 1.260 | 0.06018 | 590.0 | 1.22 |
| <i>m</i> -Chlorophenol | 826.9 | 1.249 | 0.04722 | 459.0 | 1.49 |
| <i>o</i> -Chlorophenol | 406.7 | 1.210 | 0.02250 | 212.0 | 1.0 |
| <i>p</i> -Cresol | 1203.8 | 1.015 | 0.05607 | 527.0 | 1.62 |
| <i>m</i> -Cresol | 1091.3 | 1.014 | 0.05057 | 475.0 | 1.48 |
| <i>o</i> -Cresol | 742.7 | 1.027 | 0.03506 | 333.0 | 1.12 |
| <i>n</i> -Tolyl methyl ether | 200.6 | 0.9546 | 0.008753 | 68.5 | — |
| <i>m</i> -Tolyl methyl ether | 193.7 | 0.9589 | 0.008491 | 66.7 | — |
| <i>p</i> -Tolyl methyl ether | 185.8 | 0.9497 | 0.008064 | 62.8 | — |
| <i>o</i> -Nitrophenol | 433.5 | 1.183 | 0.02343 | 190.0 | 0.84 |
| Ethyl salicylate | 350.5 | 1.106 | 0.01772 | 118.0 | 0.9 |
| Salicylaldehyde | 320.1 | 1.141 | 0.01669 | 156.0 | — |
| Benzyl alcohol | 640.5 | 1.027 | 0.03008 | 286.0 | 1.66 |
| Benzyl acetate | 296.5 | 1.033 | 0.01390 | 96.3 | — |
| Benzyl methyl ether | 233.6 | 0.9624 | 0.01023 | 81.1 | — |
| β -Naphthol (at 130°) | 376.0 | — | — | — | — |
| α -Naphthol (at 130°) | 312.6 | — | — | — | — |

TABLE II.
Solutions in Amyl Acetate at 25°.

| Substance. | Time of flow in seconds. | Density. | Viscosity. | η Mol. vol. $\times 10^6$. |
|------------------------------|-----------------------------|----------|------------|-------------------------------------|
| Amyl acetate | 201.4 | 0.8659 | 0.008055 | — |
| Phenol | 267.1 | 0.8951 | 0.01105 | 165.0 |
| Anisole | 202.0 | 0.8856 | 0.008265 | 67.8 |
| Phenyl acetate | 223.3 | 0.9033 | 0.009319 | 61.9 |
| Phenetole | 209.6 | 0.8829 | 0.008550 | 61.4 |
| <i>p</i> -Chlorophenol | 295.9 | 0.9289 | 0.01270 | 91.8 |
| <i>m</i> -Chlorophenol | 290.3 | 0.9274 | 0.01244 | 89.8 |
| <i>o</i> -Chlorophenol | 281.1 | 0.9254 | 0.01202 | 86.5 |

TABLE II. (continued).
Solutions in Amyl Acetate at 25°.

| Substance. | Time of flow in seconds. | Density. | Viscosity. | $\frac{\eta}{\text{Mol. vol.}} \times 10^4$ |
|---------------------------------------|-----------------------------|----------|------------|---|
| <i>p</i> -Cresol | 283.4 | 0.8931 | 0.01169 | 96.7 |
| <i>o</i> -Cresol | 281.3 | 0.8964 | 0.01165 | 95.7 |
| <i>m</i> -Cresol | 282.9 | 0.8928 | 0.01167 | 95.5 |
| <i>m</i> -Tolyl methyl ether | 214.9 | 0.8847 | 0.008784 | 63.7 |
| <i>o</i> -Tolyl methyl ether | 211.7 | 0.8853 | 0.008659 | 62.8 |
| <i>p</i> -Tolyl methyl ether | 210.6 | 0.8840 | 0.008602 | 62.5 |
| <i>p</i> -Nitrophenol | 358.5 | 0.9440 | 0.01564 | 106.0 |
| <i>m</i> -Nitrophenol | 331.1 | 0.9418 | 0.01449 | 98.2 |
| <i>o</i> -Nitrophenol | 242.9 | 0.9365 | 0.01051 | 70.8 |
| * Ethyl <i>p</i> -hydroxybenzoate ... | — | 0.931 | 0.0166 | 93.0 |
| Ethyl <i>m</i> -hydroxybenzoate .. | 370.9 | 0.9261 | 0.01587 | 88.6 |
| Ethyl salicylate | 246.3 | 0.9184 | 0.01045 | 57.6 |
| Benzyl alcohol | 250.6 | 0.8943 | 0.01035 | 85.7 |
| Benzhydrol | 351.4 | 0.9212 | 0.01496 | 74.9 |
| * Triphenylcarbinol | — | 0.97 | 0.0190 | 70.0 |
| Benzyl methyl ether | 207.8 | 0.8832 | 0.008479 | 61.4 |
| Benzyl acetate | 233.6 | 0.9023 | 0.009738 | 58.6 |
| β -Naphthol | 375.5 | 0.9210 | 0.01598 | 102.0 |
| α -Naphthol | 371.2 | 0.9031 | 0.01549 | 97.1 |

* By extrapolation.

TABLE III.
The Chlorophenols in Ethyl Alcohol at 25°.

| Substance. | Time of flow in seconds. | Density. | Viscosity. | $\frac{\eta}{\text{Mol. vol.}} \times 10^4$ |
|------------------------------|-----------------------------|----------|------------|---|
| Alcohol | 309.2 | 0.7876 | 0.01125 | — |
| <i>p</i> -Chlorophenol | 364.0 | 0.8646 | 0.01454 | 97.8 |
| <i>o</i> -Chlorophenol | 364.2 | 0.8628 | 0.01452 | 97.5 |
| <i>m</i> -Chlorophenol | 363.7 | 0.8631 | 0.01450 | 97.4 |

Discussion of Results.

Table I.—The results in column 4 follow very closely those obtained by Auwers and by Hewitt and Winmill, with one exception. In two cases (the cresols and hydroxybenzoic esters), the latter authors found the order of increasing association to be ortho—meta—para, and in two other cases (the chloro- and nitro-phenols) to be ortho—para—meta, whereas Auwers in all cases found the order to be ortho—meta—para, the meta-compound approximating more nearly to the para-compound.

The viscosity results are in full agreement with those of the latter author, though it must be remembered that V. Meyer found the order of steric hindrance in the case of the esterification of substituted benzoic acids to be ortho—para—meta (*Ber.*, 1895, 28, 1254).

That the order of the viscosity results is not merely due to the position of the substituent group in the benzene nucleus apart from its influence on the hydroxyl group is shown by the fact that the values for the tolyl methyl ethers do not fall in this order.

It will be noticed that the mean value of the expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ for the ethers is 66, these compounds being practically unassociated. The value for benzene is 65 (Dunstan, *Zeitsch. physikal. Chem.*, 1905, 51, 738).

In the case of benzyl methyl ether, the slightly higher value may be due to disturbance of the symmetry of the molecule by the comparatively long side-chain. Phenyl and benzyl acetates appear to be slightly associated, this being probably due to the slight residual affinity possessed by the carbonyl oxygen atom in the acetyl group.

For benzyl alcohol and all the phenols, $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ is marked higher, indicating considerable association. Ortho-substituted phenols appear to be less associated than phenol itself, presumably owing to the proximity of the substituent to the source of association, the carboethoxyl, aldehyde, nitro-, and halogen groups exercising very considerable influence. The marked effect of these groups has been pointed out by Auwers and by Hewitt and Winnill.

The results obtained by Auwers indicate that the aldehyde group has the greatest inhibiting influence, followed in order by the carboethoxyl, the nitro-, the halogen, and finally the alkyl groups. The viscosity results, while agreeing in the main with these, invert the order of the first two groups. No satisfactory explanation of this discrepancy is apparent.

It is noteworthy that in the first four cases the ortho-substituent contains an unsaturated nucleus, and it appears probable that the latent valency of this nucleus in some way attracts part of that of the hydroxyl group, thus lessening the tendency for association. This action is, of course, supplementary to the steric hindrance produced by the ortho-substituent by virtue of its proximity to the hydroxyl group.

This explanation is rendered still more probable by the fact that the aldehyde and carboethoxyl groups, which depress association most strongly, are known to be markedly unsaturated, whilst the methyl group, which exercises only a slight inhibitive influence, is practically saturated.

An interesting parallel is observed when the molecular refractivities of various substituted benzene derivatives are considered (Smiles, *Chemical Constitution and Physical Properties*, p. 298).

| Substance. | M _a (obs.). | M _a (calc.). | Δ. | Δ due to substituent. |
|-----------------------|------------------------|-------------------------|-------|-----------------------|
| Phenylacetylene | 34.46 | 33.53 | +0.93 | +1.31 |
| Styrene | 35.98 | 35.08 | +0.90 | +1.28 |
| Benzaldehyde | 31.77 | 31.01 | +0.76 | +1.11 |
| Nitrobenzene | 32.69 | 32.10 | +0.59 | +0.97 |
| Benzonitrile | 31.32 | 30.75 | +0.57 | +0.95 |
| Aniline | 30.27 | 29.72 | +0.55 | +0.93 |
| Acetophenone | 36.00 | 35.58 | +0.42 | +0.86 |
| Methyl benzoate | 37.55 | 37.23 | +0.32 | +0.79 |
| Phenol | — | — | -0.07 | -0.21 |
| Iodobenzene | — | — | -0.24 | -0.33 |
| Bromobenzene | — | — | -0.31 | -0.47 |
| Chlorobenzene | — | — | -0.32 | -0.66 |
| Benzene | — | — | -0.38 | .. |

The degree of disturbance of the benzene system increases with the increasing degree of unsaturation of the substituent. It has also been shown, from measurements of molecular magnetic rotation (Perkin, *Trans.*, 1896, **69**, 1152), that the anomaly shown by dimethylaniline is diminished when the residual affinity of the basic group is satisfied by the addition of hydrochloric acid. A similar argument appears to explain the gradual decrease in the reactivity of the carbonyl group in the series acetone—ethyl acetate—acetic acid. In the first compound, where the carbonyl group is adjacent to two saturated methyl groups, it possesses a sufficient degree of unsaturation to combine with sodium hydrogen sulphite and with hydrogen cyanide. In ethyl acetate one of the adjacent groups is ethoxyl, the oxygen atom of which possesses a certain amount of latent affinity (compare the combination of ethyl ether with hydrogen chloride and with magnesium alkyl halides). This affinity exerts an attractive influence on part of the latent affinity of the carbonyl group, with the result that ethyl acetate will not combine with such a number of reagents as will acetone.

In acetic acid, the oxygen of the hydroxyl group possesses considerable residual affinity, part of which is united with that of the carbonyl group, which thus loses its characteristic additive properties, whilst the remainder produces association of the molecules.

Owing to the comparatively high temperature employed in working with the fused naphthols, accurate density measurements were not attainable, and only the time of flow (the chief factor in determining the viscosity) was measured. The results indicate clearly the influence of the second ring of the naphthalene nucleus in hindering the association of α -naphthol. V. Meyer observed a similar effect when measuring the velocities of esterification of 2-chloro-1-naphthoic acid and 3-chloro-2-naphthoic acid, the former compound esterifying very slowly (*Ber.*, 1895, **28**, 182).

Table II.—It should be pointed out that the results in column 1 have been obtained with solutions of an empirical concentration.

and are therefore comparable only among themselves, and not with the corresponding figures in table I.

It will be seen that the results in table I are exactly confirmed, and also that a further range of substances has been studied. In each case the phenols are associated, the ortho to the least, and the para to the greatest extent, the meta-compounds, as before, approximating more closely to the para-compounds. The gradual inhibition of the association of benzyl alcohol by the progressive replacement of the hydrogen atoms of the side-chain by phenyl groups is also clearly indicated. This, again, is in full agreement with surface energy results. Although the figures for triphenylcarbinol are obtained by extrapolation and therefore are not of the usual degree of accuracy, it is clear that this substance approximates to the ethers in its slight degree of association.

Ethyl salicylate and *o*-nitrophenol, again, show practically no signs of association.

A very striking point is the dissociating influence of the amyl acetate. This was specially chosen as a comparatively inert, non-dissociating solvent, but its effect on the associated solutes is most marked. The viscosities of the cresols in the pure state differ very considerably, but solution evidently breaks down the complexes to a large extent, and the viscosities of the solutions are almost identical. The dissociating influence is more marked in this case than in that of the other phenols, the cresol complexes being apparently more unstable than those of the other substituted phenols. If the difference between the values for $\frac{\eta}{\text{Mol. vol.}} \times 10^6$

found for ortho- and para-isomerides be taken as a measure of the relative stability of the complexes, this stability decreases in the order carbethoxyl—nitro—halogen—alkyl. The slight signs of association noticeable in the pure phenyl and benzyl acetates disappear in the amyl acetate solutions, and the substances appear to be completely dissociated.

Table III.—As it was observed that a comparatively non-dissociating solvent had such a marked disruptive effect on the molecular aggregates, it was considered of interest to determine the viscosities of solutions of a set of three isomerides in a dissociating solvent. For this purpose, solutions of the chlorophenols in ethyl alcohol were chosen, and the results indicated that practically complete dissociation had resulted. Preliminary experiments with solutions of the chlorophenols in light petroleum (one of the least dissociating of ordinary solvents) showed that the dissociation produced was less than in the case of amyl acetate, and a detailed study of the effect of various solvents on associated substances is now being carried out.

Summary of Results.

(1) The results obtained by the viscometric method agree very closely with those derived from other physical constants, such as vapour pressure, dielectric constant, molecular surface energy, molecular refractivity, and molecular weight determined cryoscopically.

(2) Viscosity determinations, using $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ as a criterion of association, show that phenols are associated, the ortho-compounds to the least, and the para-compounds to the greatest extent. The ethers are unassociated, but the acetates show slight association.

(3) The carbethoxyl, aldehyde, nitro-, and halogen groups exert a marked inhibitive influence on association. Alkyl groups only exert a slight influence. Since the degree of inhibition of association appears to be intimately connected with the degree of unsaturation of the substituent, it is suggested that the depression of association is partly due to some kind of attraction between the latent valency of the hydroxylic oxygen and the unsaturated substituent, the consequence being a diminution of the tendency to form complexes through the latent valency of the hydroxyl group. The same hypothesis explains the gradual disappearance of the characteristic reactivity of the carbonyl group in the series acetone—ethyl acetate—acetic acid.

(4) Solution in even a comparatively inert solvent, such as amyl acetate, produces considerable disruption of the molecular aggregates. In a dissociating solvent, such as ethyl alcohol, the dissociation is practically complete.

The author desires to express his sincere thanks to Dr. J. T. Hewitt and to Dr. A. E. Dunstan for the interest they have taken in the work, and to the Chemical Society for a grant which has covered the expense entailed.

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EAST HAM TECHNICAL COLLEGE.

CLXVII.—*Binary Mixtures of Some Liquefied Gases.*

By BERTRAM DILLON STEELE and L. S. BAGSTER.

THE work described in this paper was undertaken in the first place in connexion with the study of simple inorganic solvents.

Combination between solute and solvent is usually held to be a necessary antecedent to conduction, whilst the form of the vapour pressure-composition curve for mixtures of volatile substances is often accepted as evidence for or against combination in such solutions.

One of us (*Proc. Roy. Soc.*, 1904, **73**, 450) has found that mixtures of the halogen hydrides with hydrogen sulphide form solutions which do not conduct, whilst we have examined sulphur dioxide and hydrogen bromide, and found them to mix in all proportions, forming solutions which show but very slight conductivity. The hydrogen sulphide solutions are doubly interesting, owing to the analogy between hydrogen sulphide and water.

We therefore decided to examine the vapour pressure-composition curves of the solutions formed by sulphur dioxide and by hydrogen sulphide with the halogen hydrides. Hydrogen chloride solutions have not been systematically examined, owing to difficulties caused by the low boiling point of the hydrogen chloride, and to the absence of liquid air. We have, however, found from some rough experiments that sulphur dioxide at -35° dissolves hydrogen chloride to form a solution approximately normal, and that all the hydride can be removed from such a solution by fractional distillation, and therefore no constant boiling mixture can be formed at this temperature. Judging from analogy, also, one would expect the curve obtained to be of a similar type to that given by sulphur dioxide and hydrogen bromide, which pair of liquids has been systematically examined.

Mixtures of hydrogen iodide and sulphur dioxide could not be formed, owing to the fact that these substances react in the gaseous state, depositing sulphur and iodine.

It will be convenient, first, to describe the apparatus used and the method of working, following this with an account of the results obtained. For the preparation of the various hydrides used, the methods described in the paper previously mentioned have been followed. The sulphur dioxide was obtained commercially in a steel cylinder, and fractionated before use. For the preparation of the liquid hydrogen sulphide and bromide, a mixture of solid carbon dioxide and ether was used as refrigerant, liquid ammonia

being used to condense the sulphur dioxide and hydrogen iodide. In the actual experiments, liquid ammonia was used for the low temperature bath, constant temperatures from -35° to -75° being easily obtained by varying the pressure over the ammonia by means of a water pump.

Ammonia and hydrogen iodide boil at about the same temperature, but it was found that if the top of the vacuum vessel containing ammonia were left open to the air and not plugged with cotton wool, as is usual, the diminution in the partial pressure of the ammonia, brought about by air convection currents, was sufficient to lower the temperature to 10° or 15° below the boiling point of the ammonia under atmospheric pressure. The temperature thus obtained was sufficiently low to condense the hydrogen iodide, and as the carbon dioxide mixture froze the liquid in the condenser, the above method of cooling was adopted. If the temperature rose owing to heat given out by the condensing hydride, an air current occasionally blown through the ammonia by means of a foot-bellows sufficed to reduce it again.

The difficulty of measuring the vapour pressure of substances, such as the halogen hydrides, which attack mercury was overcome by using the glass spiral manometer of Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, **8**, 20), as modified by Johnson (*Zeitsch. physikal. Chem.*, 1908, **61**, 458).

It may be mentioned here that as the halogen hydrides are decomposed by organic matter, rubber tap grease was not used, being replaced by a mixture of pure paraffins. On account of the extremely hygroscopic nature of the halogen hydrides, every entrance to the apparatus by means of which moisture could gain access was protected by a phosphoric oxide tube, and as the oxide appeared to contain some impurity which slowly reacted with the halides, the tubes containing it were attached to the apparatus with taps interposed as shown in Fig. 1. The oxide was thus only exposed to the halides for short periods.

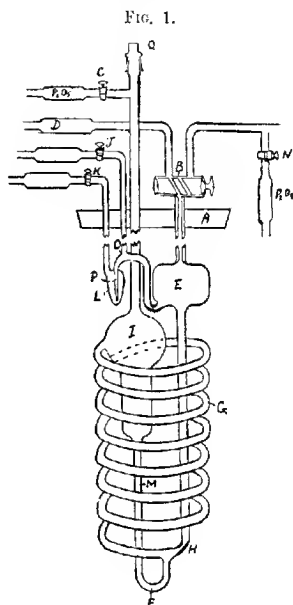
Fig. 1 shows the apparatus used. Glass was, of course, used for its construction, and all joints were sealed. The apparatus was fitted with a rubber cork J, selected to fit closely the mouth of an unsilvered, cylindrical Dewar flask. The various tubes were passed through holes in the cork, and sealed to the apparatus afterwards. In addition to the holes for the apparatus, the cork was bored to contain the thermometer, a glass tube for making connexion with a water pump for reducing the pressure over the ammonia, another tube closed by rubber tubing and a pinchcock for the admission of fresh ammonia, and a glass tube drawn to a capillary at its lower end, which reached to the bottom of the vacuum vessel, the top

being also closed by rubber tubing and a pinchcock. The purpose of this tube will be explained presently.

Between the water pump and the vessel containing the ammonia was interposed a piece of rubber pressure tubing, which could be more or less closed by means of a screw clip. To obtain any desired temperature below the boiling point of the ammonia, the pump was set in action while a stream of air was admitted through the capillary. The ammonia boiled under the reduced pressure, and its temperature fell. The air stream served to prevent superheating and subsequent bumping, and also to stir the liquid and obtain a uniform temperature throughout the bath. When the temperature was near the desired point, the pressure tubing was partly closed by means of the screw clip, thus checking the rate of withdrawal of the ammonia vapour, and consequently the rate of evaporation, so lessening the heat absorption and fall of temperature. In a short time a state of equilibrium was reached, and by this means the temperature could be kept constant to 0.1° for half an hour. If it varied, a slight turn of the screw clip occasionally sufficed to adjust it again. It was possible to run for half an hour without adding fresh ammonia.

A normal pentane thermometer, reading to -115° , was used. It was not wholly immersed, and there was a large correction for the exposed portion of the stem, which correction is probably nearly correct at the lower temperatures, but may have an error of about a degree at the higher. As our object was to work at a constant temperature rather than to know its exact value, slight errors are in our case not important, as our vapour pressure-composition curves are constructed at constant temperature.

The construction of the actual apparatus will be apparent from Fig. 1. A description of the method of working should render the use of the various parts clear.



The temperature of the ammonia-bath was reduced to well below the boiling point of the liquid it was desired to use. The liquid previously condensed in another vessel was then distilled into the apparatus through *O* and the three-way tap *B*. The first few drops of liquid condensed collected in the bend *F*, after which all uncondensed gas travelled round the spiral *G* rather than force its way against the pressure of the liquid in *F*. By this means, thorough condensation was secured. The capacity of the apparatus was known at various points, so that mixtures of any desired strength could be made up approximately by distilling in the necessary volumes of each liquid. This was more necessary in changing the composition of a previous mixture than in preparing the first one, when the volumes of liquid distilled in could, of course, be measured. About 25 c.c. of liquid were necessary to fill the apparatus to the amount necessary for its correct working.

To ensure thorough mixing of the two liquids, a hydrogen generator was connected to *D*, and hydrogen passed through *E*. When the gas reached the point *H*, it broke into bubbles, which ran around the spiral *G*, carrying liquid with them into the bulb *I*, from whence the liquid flowed back through *M*, while the gas passed out at *C*. The hydrogen pressure was now applied at *C*, the taps *B*, *J*, and *K* having been closed. These taps were then carefully opened, when the liquid rose, filling the bulbs *E* and *L*, and on reaching the warm tubes boiled and displaced the contained air. The capacities of the various parts were so arranged that when *E* and *L* were full of liquid there was still some in the spiral and tube *M*, whilst when *E* and *L* were empty the level of the liquid in *I* was above the entrance of the spiral.

Having displaced the air as described above, the manometer and its connecting tube were exhausted through the tap *N* by means of an efficient water pump, *B* being kept closed. *B* was then turned to admit vapour into the manometer. By alternately filling and exhausting the manometer several times, the air was all displaced. Suction was now applied at *C* until the liquid level was nearly at the bottom of the bulb *E*, and at this stage, after the temperature had been constant for several minutes, a vapour pressure reading was taken. The whole process described above was now repeated until the vapour pressure was constant, when the temperature was varied, and a series of vapour-pressure readings was taken. The volumes of the manometer and its connecting tube were small, and did not require much vapour to fill them, consequently the composition of the liquid would not be much changed by the exhausting process; in any case, as the readings

and subsequent samples were all taken after the exhaustion, any slight change would be of no importance.

It was found that after taking a series of vapour-pressure readings the pressure appeared to increase slightly. This was attributed to decomposition of the halide vapour by the tap grease with consequent production of hydrogen. To reduce any error caused by this, the manometer was occasionally exhausted during a series of readings. The vapour pressures were plotted against the temperatures, and from the curves the vapour pressure at any desired temperature could be calculated. These curves are referred to later in the paper.

Having obtained the vapour-pressure curve, it was necessary to obtain samples of the liquid and gas phases for analysis. For this purpose, it was necessary to isolate and absorb completely a portion of the liquid in order to get its true composition. This was accomplished by means of the bulb *L*. By means of the hydrogen pressure, the bulb *E* was filled with liquid, and by then applying pressure alternately at *C* and *K* and suitably opening the taps, *L* was alternately filled with and emptied of liquid to ensure having a true sample. Finally, a small quantity of liquid was left in *L*, and the hydrogen pressure applied at *J*, keeping the tap shut. Geissler tubes, as used for carbon dioxide absorption in combustions, were attached at *K* and *C* by rubber tubing, the taps being closed. On opening the tap *J*, the hydrogen pressure forced a few bubbles of gas into *L* and *E*, and left the connecting tube full of gas, thus separating the two portions of liquid. The taps *K* and *C* were now carefully opened. A stream of gas passed down the tube *J*, and at *O* divided into two portions. One stream bubbled through *L*, evaporating the contained liquid, which was absorbed by the alkali in the Geissler bulb attached to *K*. *P* is a fairly fine capillary tube, which served to prevent diffusion backwards of vapour from *L*. The other gas stream passed into *E* and down the tube to *H*, where it broke into bubbles at the constriction. The tube leading from *E* to *I* has a capillary constriction, which served to increase the velocity of the gas stream, and thus helped to prevent diffusion of vapour from *E* to *L*, which would cause an error in the analysis.

The bubbles of hydrogen, on forming at *H*, ran around the spiral *G*, which contained over a metre of glass tubing. These bubbles, as explained previously, caused thorough mixing of the liquid, and ensured it being of uniform composition, and at the same time became saturated with the gas phase in equilibrium with the liquid. Finally, the hydrogen saturated with the vapour passed through the tap *C* and through the attached Geissler bulb, where absorbable

gases were collected. A little experience showed how much liquid it was necessary to have in *I*, in order to obtain convenient analytical results, and also how long to pass the hydrogen through the spiral to get the gas composition.

When the absorption was complete, each Geissler bulb was removed, and its contents thoroughly mixed by blowing them from one bulb to the other. The solution was then blown into a beaker, and as only ratios were required it was not necessary to remove the whole contents, but it was necessary to have them thoroughly mixed before removal. Aliquot parts of the solution were removed for analysis by means of pipettes, the necessary volumes for convenient titration values being judged from knowledge of the approximate composition of the mixtures and from previous analyses.

Sulphur dioxide and hydrogen sulphide were determined by titration with $N/10$ iodine solution, and the halogen hydrides by Volhard's method, using $N/10$ silver nitrate and potassium thiocyanate. As silver sulphide is not easily dissolved by nitric acid, it was necessary to remove hydrogen sulphide from solutions before estimating the halogen. This was done by oxidation with sodium peroxide and subsequent removal of excess of hydrogen peroxide by boiling. The quantities of gas removed for an analysis were insufficient to change appreciably the composition of the liquid remaining. A series of analyses of each liquid was made at different temperatures, thus obtaining a series of values for the composition of the liquid which should agree, and other values for the composition of the gas which should either agree or show regular variation with temperature.

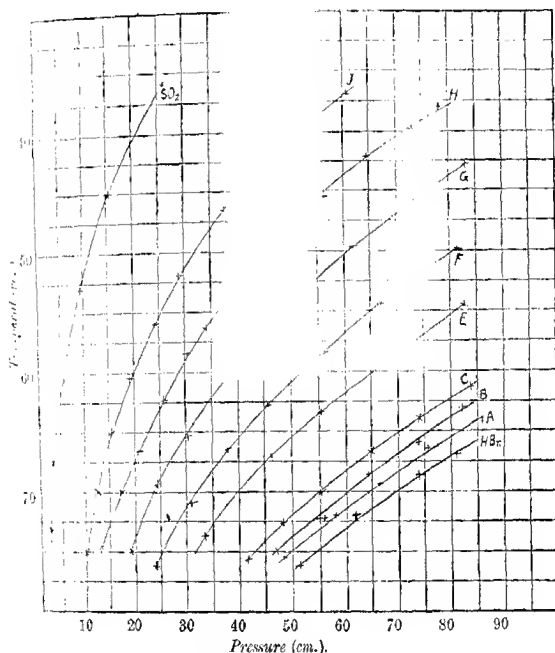
To prepare a fresh mixture, the cap *Q* was removed, a fine glass tube passed into *I*, and a portion of the liquid sucked out by means of a water pump. The cap was then replaced, and fresh liquid distilled in.

The apparatus was contained in a vacuum vessel measuring about 4.5 cm. by 20 cm., internal dimensions.

The apparatus we have described could be made on a larger scale if the liquids to be used were more easily prepared and less expensive. It might be useful at the ordinary temperature for liquids which are hygroscopic or decomposed by air. If used on the larger scale, it could be applied to liquids which cannot be directly absorbed or estimated, sufficient liquid being used to allow a quantity sufficient for analysis by physical measurements to be distilled out and condensed without appreciably changing the composition of the residue. With modern means of obtaining low temperatures, even very volatile substances might be thus condensed.

*Exper**results.*

The experimental results are given in the following tables. For several reasons it was not possible to obtain data for the construction of complete vapour pressure-composition curves over a limited range of temperature. The analyses could not be performed when the vapour pressure of the solution was greater than



Sulphur dioxide—hydrogen bromide.

atmospheric, whilst, owing to the differences in the boiling points of the two constituent mixtures rich in the less volatile constituent, they could be analysed at a higher temperature than those containing more of the more volatile constituent. A lower limit was fixed by the lowest temperature that could be conveniently obtained with the liquid ammonia, whilst with the hydrogen iodide a limit was fixed by the freezing of solutions rich in that compound.

A vapour pressure-composition curve has been constructed for each pair of liquids at that temperature at which most complete data are available.

Portions of curves for other temperatures can be constructed from the data given.

Sulphur Dioxide and Hydrogen Bromide.

Table I gives the vapour-pressure readings for mixtures of sulphur dioxide and hydrogen bromide, whilst in table II is given, as a typical example, the results of the analyses of mixture *F*. The vapour pressure-temperature curves are shown in Fig. 2. The letters at the heads of the columns of tables I and II and the curves in Fig. 2 all refer to the same mixtures. Pressures are given in cm. of mercury. All compositions of mixtures are expressed as molecular percentages of halogen hydride.

TABLE I.

| Mixture. | Temp. | -76° | -72° | -68.6° | -66.8° | |
|-----------------|-------|--------|--------|--------|--------|------------------------------------|
| HBr | V. P. | 51.7 | 61.7 | 73.9 | 80.9 | |
| A. | Temp. | -75.5° | -72° | -69.3° | -66.4° | -64.3 |
| | V. P. | 48.5 | 57.9 | 66.4 | 75.7 | 85.8 |
| B. | Temp. | -75° | -72.3° | -68.6° | -65.9° | -63° |
| | V. P. | 40.9 | 55.8 | 64.4 | 73.8 | 82.1 |
| C. | Temp. | -75.7° | -72.6° | -70° | -66.7° | -63.9° -61.3° |
| | V. P. | 41.6 | 48.2 | 55.2 | 65.0 | 74.1 83.5 |
| E. | Temp. | -73.7° | -67.1° | -63.5° | -58.5° | -54.6° |
| | V. P. | 33.0 | 46.2 | 55.1 | 70.1 | 82.5 |
| F. | Temp. | -76.0° | -71° | -66.5° | -62.7° | -58.5° -54.4° -49.8° |
| | V. P. | 24.1 | 30.7 | 37.9 | 45.8 | 56.0 66.7 81.5 |
| G. | Temp. | -75.0° | -69.3° | -65.3° | -59.6° | -54.2° -49.8° -46.0° -42.6° |
| | V. P. | 19.0 | 24.6 | 30.4 | 39.3 | 50.6 61.8 72.8 82.9 |
| II. | Temp. | -75.1° | -70.0° | -66.5° | -62.4° | -58.5° -56.3° -53.5° -49.4° |
| | V. P. | 14.0 | 17.2 | 21.0 | 25.8 | 30.5 34.1 38.6 40.6 |
| | Temp. | -45.6° | -42.1° | -39.3° | -38.0° | |
| | V. P. | 56.4 | 64.5 | 73.1 | 78.1 | |
| J. | Temp. | -75.0° | -70.0° | -63.0° | -60.3° | -55.9° -52.0° -46.6° -41.4° -37.6° |
| | V. P. | 10.0 | 12.3 | 15.3 | 19.2 | 24.1 29.0 37.7 43.6 60.7 |
| SO ₂ | Temp. | -73.0° | -67.3° | -60.3° | -53.0° | -45.0° -36.0° |
| | V. P. | 2.1 | 3.0 | 5.8 | 9.4 | 15.2 26.0 |

TABLE II.

| Mixture. | Temperature. | Molecular percentage of HBr (liquid). | | Molecular percentage of HBr (gas). | |
|------------|--------------|---------------------------------------|--|------------------------------------|----|
| | | Value used. | | Value at -65°. | |
| <i>F</i> . | -75° | 28.5 | | 35.3 | |
| | -67.5 | 30 | | 94.3 | 94 |
| | -60.3 | 29 | | 93.1 | |
| | -53 | 28.5 | | 92.2 | |

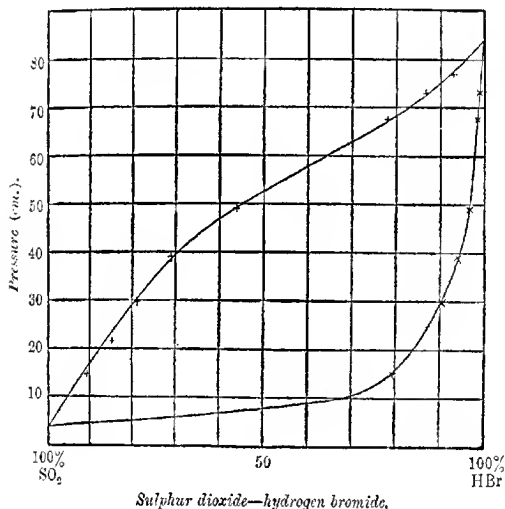
The samples of gas and liquid were usually taken first at the lowest temperature, then at the highest, followed by others at

intermediate temperatures. An examination of table II shows that the temperature has a distinct effect on the composition of the gas, increasing temperature causing an increase in the relative quantity of sulphur dioxide in the gas phase.

The vapour pressure-concentration curve has been drawn for a temperature of -66° , and is shown in Fig. 3. If necessary, the gas composition at this temperature was calculated from the values at surrounding temperatures.

At lower temperatures the points do not fit so well to the curves, which, however, appear to conform to the same type. The type of

FIG. 3.



curve is well known, and is of the general shape one might expect from a knowledge of the properties of the constituents and of the mixtures. The partial pressure curves have not been drawn. That for hydrogen bromide will nearly correspond with the total pressure curve, whilst the sulphur dioxide curve will lie almost along the line of zero pressure.

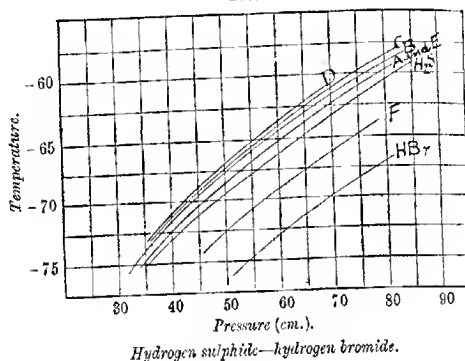
Hydrogen Sulphide and Hydrogen Bromide.

Table III contains the vapour-pressure readings for mixtures of hydrogen sulphide and hydrogen bromide. As before, pressures

are given in cm. of mercury, and compositions of mixtures are expressed as molecular percentages of halogen hydride.

The vapour pressure-temperature curves are shown in Fig. 4. As the curves lie so closely together, the points through which they were drawn are not marked. Reference to the tables will show that the points fit the curves closely. By chance, mixtures *A* and *E* have the same vapour pressure, and are represented by the same curve

FIG. 4.



AE. The curves show that a mixture of minimum vapour pressure and consequent maximum boiling point is formed.

TABLE III.

| Mix- ture. | | | | | | | | | |
|------------------|-------|--------|--------|--------|--------|--------|--------|--------|--------------|
| H ₂ S | Temp. | -75.1° | -73.1° | -71.0° | -69.0° | -66.6° | -65.0° | -63.0° | -61.0° -59.3 |
| | V. P. | 35.3 | 39.8 | 45.6 | 52.6 | 58.6 | 64.5 | 70.9 | 77.6 83.1 |
| <i>A.</i> | Temp. | -75.0° | -72.7° | -70.0° | -67.5° | -65.0° | -62.2° | -59.5° | |
| | V. P. | 34.9 | 39.5 | 46.8 | 53.2 | 60.6 | 70.6 | 81.5 | |
| <i>B.</i> | Temp. | -75.4° | -71.7° | -67.6° | -64.4° | -60.9° | -58.5° | | |
| | V. P. | 32.6 | 39.6 | 50.1 | 59.9 | 72.7 | 83.0 | | |
| <i>C.</i> | Temp. | -75.0° | -72.0° | -68.2° | -64.6° | -60.1° | -58.0° | | |
| | V. P. | 33.8 | 38.7 | 47.7 | 58.4 | 73.6 | 82.2 | | |
| <i>D.</i> | Temp. | -72.7° | -64.0° | | | | | | |
| | V. P. | 36.0 | 58.1 | | | | | | |
| <i>E.</i> | Temp. | -74.2° | -69.0° | -65.7° | -60.9° | | | | |
| | V. P. | 36.3 | 49.0 | 58.9 | 76.2 | | | | |
| <i>F.</i> | Temp. | -74.1° | -72.0° | -69.0° | -63.8° | | | | |
| | V. P. | 46.4 | 51.2 | 60.7 | 78.3 | | | | |

The gas composition was not so regular as with the sulphur dioxide mixtures, and, as a rule, the mean value has been taken in constructing the vapour pressure-concentration curve, which has been drawn for -70° (Fig. 5). The minimum referred to is well shown.

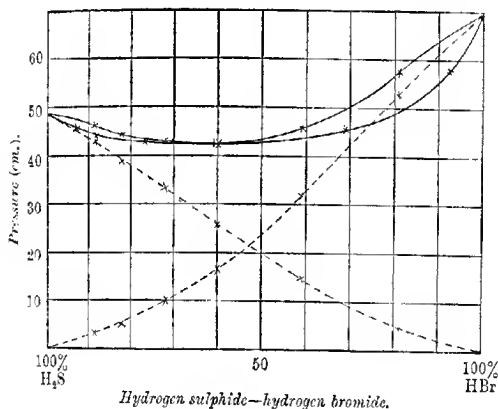
Ostwald has pointed out that in all cases the partial pressure curves of the components of a binary mixture must be symmetrical, being, in fact, mirror images of each other except as regards vertical measure. The partial pressure curves of hydrogen bromide and hydrogen sulphide, which are shown by dotted lines in Fig. 5, furnish an example of this.

Hydrogen Sulphide and Hydrogen Iodide.

Table IV gives the vapour-pressure readings for the mixtures of hydrogen sulphide and hydrogen iodide. The vapour pressure-composition curves are shown in Fig. 6.

Reference to Fig. 6 will show that the vapour-pressure measure-

FIG. 5.



nents for pure hydrogen iodide have not been carried below the freezing point, which is about -52.5° by the thermometer used.

Owing to the higher vapour pressure of the hydrogen sulphide, it was necessary to work at temperatures not much above -60° with mixtures rich in that constituent. To plot the complete vapour pressure-composition curve at -60° , we required the vapour pressure, not of solid hydrogen iodide, but of the supercooled liquid. This was obtained by extrapolation, the extrapolated portion of the curve being shown by the broken line.

Two separate series of experiments were performed with these substances, and are given in the tables as series I and series II.

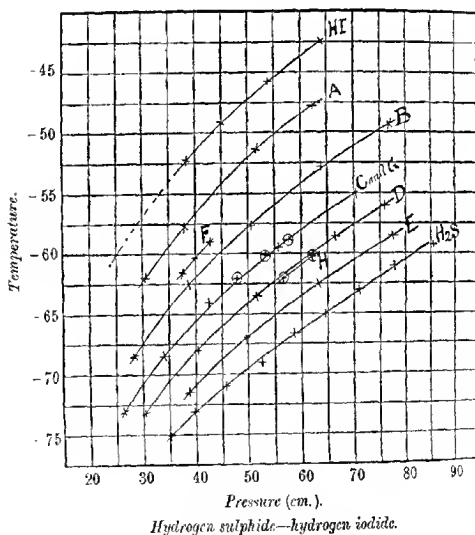
TABLE IV.—*Series I.*

| | | | | | |
|----------|-------|--------|--------|--------|--------|
| Mixture. | | | | | |
| HI. | Temp. | -39.5° | -43.0° | -45.8° | -49.2° |
| | V. P. | 74.3 | 63.8 | 53.9 | 45.0 |
| A. | Temp. | -62.0° | -57.7° | -51.3° | -47.8° |
| | V. P. | 30.5 | 37.9 | 51.6 | 62.4 |
| B. | Temp. | -68.4° | -62.5° | -57.6° | -52.8° |
| | V. P. | 28.5 | 38.6 | 50.7 | 63.7 |
| C. | Temp. | -73.0° | -68.4° | -64.0° | -59.5° |
| | V. P. | 28.4 | 34.3 | 42.3 | 55.6 |
| D. | Temp. | -78.0° | -68.0° | -63.5° | -58.5° |
| | V. P. | 30.2 | 40.4 | 51.5 | 66.6 |
| E. | Temp. | -71.5° | -67.0° | -62.5° | -58.5° |
| | V. P. | 38.8 | 49.6 | 63.1 | 77.3 |

TABLE V.—*Series II.*

| | | | | |
|----------|-------|--------|--------|--------|
| Mixture. | | | | |
| F. | Temp. | -61.5° | -60.3° | -59.0° |
| | V. P. | 37.6 | 40.0 | 42.9 |
| G. | Temp. | -62.0° | -60.2° | -58.8° |
| | V. P. | 48.0 | 53.4 | 57.6 |
| H. | Temp. | -62.0° | -60.2° | — |
| | V. P. | 56.6 | 62.0 | — |

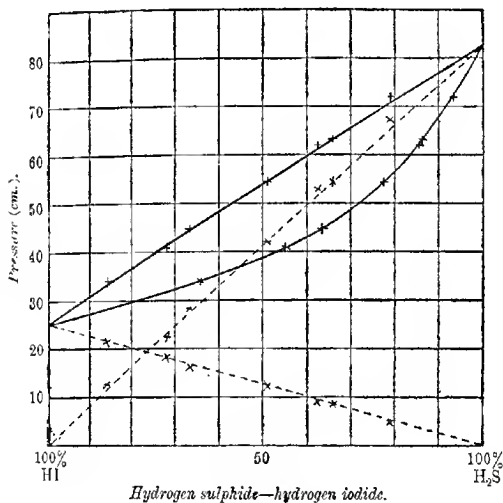
FIG. 6.



The vapour pressure composition curve at -60° is shown in Fig. 7. The partial pressure curves are shown by the dotted lines

A comparison of Figs. 5 and 7 shows a surprising contrast in the nature of the curves obtained when hydrogen bromide and hydrogen iodide respectively are mixed with hydrogen sulphide. In the case of the former substance (Fig. 5), a well-marked minimum of vapour pressure is found. The occurrence of a minimum such as this is characteristic of a few pairs of substances, the majority of which, such as the mixtures of water with the mineral acids, present as their most striking characteristic the formation of highly ionised mixtures.* Other systems presenting the same type of vapour pressure-concentration curves are mixtures of a few nitrogen bases

FIG. 7.



with fatty acids, and in the case of these there is no doubt that combination occurs to a large extent.

Roozeboom has pointed out that in nearly all cases where such minima occur we have independent evidence of (a) ionisation of one component, (b) combination between the components, or (c) association of one or both components.

From this point of view the behaviour of this pair of substances is the more remarkable, since there is no evidence of appreciable ionisation in any of the mixtures, and measurements of the molecular surface energy which were made by Steele, McIntosh, and Archibald yielded no evidence of association either of hydrogen sulphide or

of hydrogen bromide, and did not point to any difference in the molecular complexity of hydrogen bromide and hydrogen iodide. Of the three alternatives suggested by Roozeboom, there remains therefore only the possibility of compound formation between hydrogen bromide and hydrogen sulphide, and of this no evidence is yet forthcoming.

The system hydrogen sulphide and hydrogen iodide is interesting as adding another to the very short list of pairs of liquids which form ideal solutions, solutions for which Raoult's law applies over the whole range of concentration. This is shown in Fig. 7 by the occurrence of straight lines for the vapour pressure-liquid concentration curve, and for the two partial pressure curves.

In conclusion, we desire to state that the greater part of the expense of the investigation has been defrayed by a grant from the Royal Society. We also wish to express our indebtedness to Messrs. Felton, Grimwade & Co., of Melbourne, for their kindness in presenting us with considerable quantities of liquefied ammonia, and to Mr. H. J. Grayson, of this University, who specially ruled the micrometer scale which we have employed.

THE UNIVERSITY,
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CCLXVIII.—*The Volume of a Solute in Solution.*

By DAN TYRER.

THE changes of volume which occur when substances dissolve are of interest as affording valuable criteria of the nature of solutions. This study has, however, in the past been nearly always concerned with aqueous, and less frequently with alcoholic, solutions, which we now know to be abnormal in the sense that in such cases we are not dealing with simple molecular mixtures of solute and solvent. It is only in the case of very dilute aqueous solutions of salts, where the solute is practically totally dissociated, and in the case of aqueous solutions of non-electrolytes, that any regularities have been discovered.

Valson (*Compt. rend.*, 1871, 73, 441) found that the difference between the volumes of two salts M_1R and M_2R in dilute solutions is constant—independent of the nature of the acid radical R ; Nicol (*Chem. News*, 1882, 45, 37) discovered practically the same thing. Taking into consideration the degree of ionisation, Traube (*Ber.*, 1894,

27, 3173) has been able to determine what he terms the "atomic solution volumes" of most of the elements, and has shown that most of the monatomic metals have the same volume in dilute solution. In several cases of non-electrolytes in water, it has been found that the volume of the solute in solution is constant—independent of the concentration. For example, Wanklyn (*Chem. News*, 1892, 65, 122) found this to be the case for aqueous sugar solutions (see also Traube, *Annalen*, 1896, 290, 43).

In general, however, it is found that with aqueous and alcoholic solutions the specific volume of the solute in solution diminishes with increase of dilution (Gerlach, *Zeitsch. anal. Chem.*, 1888, 28, 466; Schröder, *J. Russ. Phys. Chem. Soc.*, 1886, 18, 25; Tammann and Hirschberg, *Zeitsch. physikal. Chem.*, 1894, 13, 543; Traube, *Annalen*, 1896, 290, 43). This diminution is probably due partly to ionisation and partly to changes in molecular complexes, such as the formation of solvates and variations in the molecular complexity of the solvent. In most cases of aqueous solution, the volume change brought about by the dissolution of the solute is a positive quantity, but in a few cases it has a negative value, for example, copper sulphate and sodium citrate.

On the other hand, with non-associated solvents and solutes very little work has been done.

Beilby (*Trans.*, 1883, 43, 138) found that the specific volume of paraffin wax dissolved in the paraffin hydrocarbons was approximately equal to the specific volume which the melted paraffin wax would have at the same temperature. Lumsden (*Trans.*, 1907, 91, 24) examined the change in molecular volume of several solutes dissolved in several organic solvents with change of temperature, and found that the volume increased quite regularly to temperatures above the melting points or boiling points of the pure solvent.

Forch (*Ann. Physik*, 1905, [iv], 17, 1012) determined the molecular volume of naphthalene in several solvents, such as benzene, chloroform, etc., and found that the molecular volume was constant—independent of the concentration and of the solvent (except in the case of ether), and equal approximately to the calculated molecular volume which liquid naphthalene would have at the same temperature.

Dawson (this vol., pp. 1041, 1896) found almost exactly the same thing for solutions of naphthalene and iodine in various organic solvents. The influence of the solvent was found to be rather considerable, however, in the second case, and this was considered as probably due to the formation of molecular complexes.

The object of the present work is to extend the above observations to other cases, to ascertain whether the volume in solution of a given

mass of a solute is independent of the concentration, and to what extent it is independent of the solvent.

Method and Apparatus.

Two methods have been used for measuring the specific volume of the solutions, the dilatometrical and the pycnometrical.

The dilatometer consisted of a glass bulb of about 40 c.c. capacity blown on the end of a long tube carefully graduated in mm. It was calibrated by weighing it filled with boiled distilled water (cooled in a vacuum) to various points on the stem. By this means the dilatometer was calibrated for every cm. reading along the stem. To determine the correction for the thermal expansion of the dilatometer itself, the calibrations were repeated at various other temperatures. Finally, these results were confirmed by substituting pure distilled mercury for the water and repeating the observations. All the weighings were reduced to a vacuum, and corrections were made for the curved surface of liquid in the stem of the dilatometer. The instrument was recalibrated repeatedly throughout the course of the experiments, and the slight changes which were found to have occurred were taken into account. With fairly volatile liquids, such as benzene, an appreciable quantity of the substance exists in the state of vapour in the stem. To diminish this and at the same time to prevent loss by evaporation during the course of an experiment, the open end of the stem was closed by a thin glass rod which was made to slide up and down within the stem, and could be gradually raised as the liquid expanded and rose up the stem.

The dilatometer was heated in a large bath of water, insulated from draughts. The temperature could be easily controlled to 0.01 for a time sufficient to allow the temperature of the liquid in the dilatometer to reach equilibrium. The bath was stirred with a vertically acting stirrer worked with a small motor. Two thermometers were used, both graduated in 1/10ths of a degree and readable to 1/100ths, one over a range of 0° to 50°, the other from 50° to 100°. The thermometers were calibrated to 0.01° by comparison with a standard, and the calibrations were repeated at frequent intervals throughout the course of the experiments and corrections made for any slight variations observed. All the readings of the dilatometer and thermometers were made with the help of a small telescope.

Each solution used was prepared by direct weighing of the solute and solvent, great care being taken to prevent loss by evaporation.

Details in regard to purity of the materials are given as they arise.

The observed results were made at irregular intervals of temperature (usually every 5 or 6 degrees) between 15° and a short distance

below the boiling point of the pure solvent. In order to obtain comparable results, the experimental values were plotted on a large sheet of cross section paper, of a sufficient scale to permit of readings of specific volumes to 0.00005. The mean probable error in the specific volume determinations by the dilatometer is, however, more than this, being about 0.0001. This degree of accuracy is not sufficient for very dilute solutions, and therefore experiments with the dilatometer have been confined to solutions of a moderate concentration.

If A is the percentage concentration of a solution (grams of solute per 100 of solvent), S_1 the specific volume of that solution, and S_0 the specific volume of the pure solvent at the same temperature, then the change in volume due to dissolution of A grams of the solute is $(100 + A)S_1 - 100S_0$, and the specific volume of solute in the solution is

$$v = \frac{(100 + A)S_1 - 100S_0}{A}.$$

The values of v at various temperatures have been found by the dilatometer for two cases—phenanthrene and *m*-dinitrobenzene in various solvents.

The following solvents have been used: (a) Benzene, (b) toluene, (c) acetic ester, (d) chloroform, (e) carbon tetrachloride.

The "pure" substances, obtained from Kahlbaum, were redistilled or recrystallised several times before using.

The Specific Volume (v) of Phenanthrene in Various Solvents.

The phenanthrene used was Kahlbaum's. To test its purity a small sample was recrystallised, and the melting point carefully determined. It was found to melt at the same temperature as the original specimen.

In the following table are given the values of the specific volumes of solutions of phenanthrene at various concentrations in the several solvents, with the calculated specific volumes (v) in solution:

A = percentage concentration of solution (grams solute per 100 grams solvent).

S_0 = specific volume of pure solvent.

S_1 = specific volume of solution.

v = specific volume of the solute in solution.

T = temperature.

In Benzene.

| <i>T.</i> | <i>S₀</i> | <i>A</i> = 4.199. | | <i>A</i> = 7.797. | | <i>A</i> = 15.594. | |
|-----------|----------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| | | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> |
| 15° | 1.1307 | 1.1214 | 0.899 | 1.1135 | 0.892 | — | — |
| 20 | 1.1379 | 1.1282 | 0.895 | 1.1202 | 0.893 | 1.1039 | 0.859 |
| 30 | 1.1521 | 1.1419 | 0.895 | 1.1336 | 0.896 | 1.1164 | 0.891 |
| 40 | 1.1664 | 1.1556 | 0.899 | 1.1471 | 0.899 | 1.1292 | 0.895 |
| 50 | 1.1810 | 1.1699 | 0.907 | 1.1610 | 0.904 | 1.1420 | 0.896 |
| 60 | 1.1962 | 1.1847 | 0.911 | 1.1751 | 0.905 | 1.1551 | 0.898 |
| 70 | 1.2122 | 1.1997 | 0.901 | — | — | 1.1697 | 0.902 |

In Toluene.

| <i>T.</i> | <i>S₀</i> | <i>A</i> = 3.197. | | <i>A</i> = 5.493. | | <i>A</i> = 11.712. | | <i>A</i> = 27.267. | |
|-----------|----------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| | | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> |
| 15° | 1.1458 | 1.1407 | 0.886 | 1.1348 | 0.881 | 1.1207 | 0.881 | 1.0918 | 0.853 |
| 20 | 1.1551 | 1.1467 | 0.886 | 1.1408 | 0.882 | 1.1264 | 0.881 | 1.0970 | 0.854 |
| 30 | 1.1678 | 1.1590 | 0.885 | 1.1530 | 0.883 | 1.1381 | 0.884 | 1.1078 | 0.857 |
| 40 | 1.1806 | 1.1716 | 0.890 | 1.1652 | 0.885 | 1.1500 | 0.889 | 1.1189 | 0.861 |
| 50 | 1.1936 | 1.1843 | 0.891 | 1.1778 | 0.889 | 1.1622 | 0.893 | 1.1300 | 0.867 |
| 60 | 1.2071 | 1.1975 | 0.897 | 1.1907 | 0.893 | 1.1746 | 0.897 | 1.1414 | 0.901 |
| 70 | 1.2212 | 1.2113 | 0.901 | 1.2043 | 0.897 | 1.1874 | 0.899 | 1.1530 | 0.903 |

In Acetic Ester.

| <i>T.</i> | <i>S₀</i> | <i>A</i> = 6.922. | | <i>A</i> = 9.149. | | <i>A</i> = 18.632. | |
|-----------|----------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| | | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> |
| 15° | 1.1022 | 1.0923 | 0.949 | 1.0828 | 0.869 | — | — |
| 20 | 1.1101 | 1.0988 | 0.937 | 1.0907 | 0.867 | 1.0726 | 0.873 |
| 30 | 1.1259 | 1.1143 | 0.946 | 1.1040 | 0.865 | 1.0852 | 0.868 |
| 40 | 1.1416 | 1.1296 | 0.956 | 1.1185 | 0.866 | 1.0987 | 0.871 |
| 50 | 1.1580 | 1.1452 | 0.961 | 1.1335 | 0.860 | 1.1123 | 0.872 |
| 60 | 1.1750 | 1.1616 | 0.967 | 1.1493 | 0.863 | 1.1273 | 0.874 |
| 70 | 1.1933 | — | — | — | — | 1.1426 | 0.874 |

In Carbon Tetrachloride.

| <i>T.</i> | <i>S₀</i> | <i>A</i> = 2.873. | | <i>A</i> = 4.575. | |
|-----------|----------------------|----------------------|-----------|----------------------|-----------|
| | | <i>S₁</i> | <i>v.</i> | <i>S₁</i> | <i>v.</i> |
| 15° | 0.6241 | 0.6306 | 0.858 | 0.6347 | 0.866 |
| 20 | 0.6276 | 0.6344 | 0.874 | 0.6384 | 0.875 |
| 30 | 0.6349 | 0.6421 | 0.891 | 0.6460 | 0.891 |
| 40 | 0.6430 | 0.6499 | 0.892 | 0.6538 | 0.891 |
| 50 | 0.6512 | 0.6579 | 0.891 | 0.6616 | 0.890 |
| 60 | 0.6596 | 0.6661 | 0.893 | 0.6697 | 0.890 |
| 70 | 0.6685 | 0.6746 | 0.889 | 0.6781 | 0.888 |

It will be seen from the above tables that the values of *v*, as a rule, increase slightly, but regularly, with increase in temperature. The values in acetic ester, however, show some small variations from this rule, and these are repeated (as will be pointed out later) in other cases. The effect of concentration on the value of *v* seems very slight, except, again, in the case of acetic ester. Small divergences appear with the

more dilute solutions, but here it is to be considered that the experimental error in the value of (v) is much greater than in the more concentrated solutions. For example, an error of 0.0001 in the specific volume of the solution for a concentration of 4 per cent. makes an error of about 0.004 in the value of v . Again, most of the values of the specific volume of the solutions for temperatures of 15° and 70° have been obtained by extrapolation, and therefore, in some cases, the experimental error may be greater than the average.

The influence of the solvent seems slight, but appreciable. The values of v in benzene, for example, are distinctly higher than those in toluene and carbon tetrachloride.

The Specific Volume of m-Dinitrobenzene in Various Solvents.

In Benzene.

| T. | A = 4.823 | | A = 8.939 | | A = 16.230 | |
|-----|-----------|-------|-----------|-------|------------|-------|
| | S_1 | v | S_1 | v | S_1 | v |
| 15° | 1.1101 | 0.682 | — | — | 1.0684 | 0.684 |
| 20 | 1.1109 | 0.683 | 1.1002 | 0.678 | 1.0746 | 0.685 |
| 30 | 1.1304 | 0.680 | 1.1132 | 0.678 | 1.0871 | 0.686 |
| 40 | 1.1441 | 0.682 | 1.1267 | 0.681 | 1.0997 | 0.689 |
| 50 | 1.1581 | 0.683 | 1.1403 | 0.684 | 1.1126 | 0.690 |
| 60 | 1.1724 | 0.681 | 1.1544 | 0.686 | 1.1258 | 0.692 |
| 70 | — | — | 1.1689 | 0.684 | 1.1395 | 0.692 |

In Toluene.

| T. | A = 4.092 | | A = 7.675 | | A = 15.595 | |
|-----|-----------|-------|-----------|-------|------------|-------|
| | S_1 | v | S_1 | v | S_1 | v |
| 15° | — | — | 1.1143 | 0.665 | 1.0840 | 0.668 |
| 20 | 1.1354 | 0.654 | 1.1203 | 0.667 | 1.0895 | 0.669 |
| 30 | 1.1477 | 0.656 | 1.1323 | 0.670 | 1.1009 | 0.672 |
| 40 | 1.1601 | 0.659 | 1.1444 | 0.672 | 1.1124 | 0.675 |
| 50 | 1.1726 | 0.658 | 1.1567 | 0.675 | 1.1241 | 0.678 |
| 60 | 1.1856 | 0.659 | 1.1694 | 0.679 | 1.1361 | 0.681 |
| 70 | 1.1982 | — | 1.1824 | 0.677 | 1.1484 | 0.680 |

In Acetic Ester.

| T. | A = 3.722 | | A = 6.416 | | A = 16.508 | |
|-----|-----------|-------|-----------|-------|------------|-------|
| | S_1 | v | S_1 | v | S_1 | v |
| 15° | — | — | 1.0768 | 0.679 | — | — |
| 20 | 1.0945 | 0.676 | 1.0837 | 0.672 | 1.0478 | 0.670 |
| 30 | 1.1093 | 0.665 | 1.0983 | 0.668 | 1.0612 | 0.669 |
| 40 | 1.1246 | 0.668 | 1.1132 | 0.670 | 1.0749 | 0.671 |
| 50 | 1.1404 | 0.668 | 1.1287 | 0.672 | 1.0890 | 0.671 |
| 60 | 1.1569 | 0.671 | 1.1448 | 0.673 | 1.1036 | 0.671 |

In Chloroform.

| <i>T.</i> | <i>S₀.</i> | <i>A</i> = 2.964 | | <i>A</i> = 7.017 | |
|-----------|-----------------------|-----------------------|-----------|-----------------------|-----------|
| | | <i>S₁.</i> | <i>v.</i> | <i>S₁.</i> | <i>v.</i> |
| 15° | 0.6683 | 0.6677 | 0.649 | 0.6678 | 0.668 |
| 20 | 0.6726 | 0.6721 | 0.657 | 0.6718 | 0.661 |
| 30 | 0.6812 | 0.6806 | 0.661 | 0.6801 | 0.664 |
| 40 | 0.6902 | 0.6895 | 0.664 | 0.6886 | 0.665 |
| 50 | 0.6995 | 0.6984 | 0.659 | 0.6974 | 0.667 |
| 60 | 0.7092 | 0.7075 | 0.648 | 0.7061 | 0.662 |

m-Dinitrobenzene is probably not so "normal" a substance as phenanthrene, for the nitro-compounds show, as a rule, an appreciable amount of molecular association. It will be noticed from the above tables that in all the solvents there is a slight increase in the specific volume of the solute in solution with increase of concentration, and the values of *v* vary more than in the case of phenanthrene from one solvent to another.

Determinations with the Pyknometer.

Two pyknometers have been used, one of small volume (about 5.2 c.c.) for large concentrations, and the other (about 14.5 c.c.) for the more dilute solutions. Both pyknometers were made of fused quartz, pyknometers of this material possessing the great advantage over glass instruments of changing only very slightly in volume when heated, and of being much less soluble in water. They were provided with small ground glass caps for the ends of the capillary tubes. Their volumes were determined to 0.0001 c.c. by weighing them filled with air-free distilled water at 25°, taking the specific volume of water at this temperature to be 1.002937. All the determinations were made at the constant temperature of 25.00°, the pyknometers being immersed in a large volume of water maintained at this temperature by a sensitive thermoregulator. The weighings of the pyknometer filled with the solutions were made to 0.0001 gram. Every solution investigated was made up by direct weighing of solute and solvent, and to diminish the error introduced by the unavoidable loss by evaporation of a slight amount of the solvent, several times more solution was prepared than was necessary to fill the pyknometer. All the weighings were reduced to a vacuum. The mean probable error in the specific volume determinations by the smaller pyknometer is about 0.00006, and with the larger pyknometer about 0.00002. When the concentration of the solution was more than about 8 per cent., the specific volume was determined with the small pyknometer; for smaller concentrations the larger pyknometer was used.

In the following tables are given the results of the determinations

for the constant temperature of 25·00° of several solutes in various solvents and at various concentrations.

The Specific Volume of p-Dibromobenzene in Various Solvents at 25·00°.

In the following tables:

A = percentage concentration of the solution.

S_1 = specific volume of solution at 25·00°.

v = specific volume of solute in solution at 25·00°.

S_0 = specific volume of solvent at 25·00°.

In Benzene ($S_0 = 1·14497$).

| A . | S_1 . | v . |
|--------|---------|-------|
| 5·067 | 1·11453 | 0·513 |
| 9·563 | 1·08853 | 0·516 |
| 22·935 | 1·02689 | 0·512 |
| 37·895 | 0·97129 | 0·514 |

In Toluene ($S_0 = 1·16094$).

| A . | S_1 . | v . |
|--------|---------|-------|
| 3·919 | 1·13635 | 0·508 |
| 8·395 | 1·11054 | 0·508 |
| 15·782 | 1·07155 | 0·505 |
| 30·966 | 1·00682 | 0·509 |

In Acetic Ester ($S_0 = 1·11794$).

| A . | S_1 . | v . |
|--------|---------|-------|
| 3·268 | 1·09769 | 0·479 |
| 5·569 | 1·08516 | 0·499 |
| 7·642 | 1·07443 | 0·505 |
| 14·097 | 1·04233 | 0·506 |
| 25·167 | 0·99555 | 0·508 |

In Chloroform ($S_0 = 0·67688$).

| A . | S_1 . | v . |
|-------|---------|-------|
| 2·222 | 0·67323 | 0·507 |
| 4·355 | 0·66965 | 0·505 |
| 9·973 | 0·66135 | 0·505 |

*In Carbon Tetrachloride
($S_0 = 0·63121$).*

| A . | S_1 . | v . |
|-------|---------|-------|
| 2·615 | 0·62809 | 0·508 |
| 7·710 | 0·62230 | 0·507 |

*In Ethyl Bromide
($S_0 = 0·69521$).*

| A . | S_1 . | v . |
|-------|---------|-------|
| 3·697 | 0·68808 | 0·494 |
| 4·008 | 0·68762 | 0·496 |

*In Carbon Disulphide
($S_0 = 0·79638$).*

| A . | S_1 . | v . |
|--------|---------|-------|
| 3·979 | 0·78555 | 0·513 |
| 8·701 | 0·77366 | 0·512 |
| 11·087 | 0·76835 | 0·515 |

In Ethyl Ether ($S_0 = 1·41236$).

| A . | S_1 . | v . |
|--------|---------|-------|
| 2·788 | 1·38640 | 0·456 |
| 8·099 | 1·34107 | 0·461 |
| 11·461 | 1·33855 | 0·466 |
| 18·638 | 1·26362 | 0·465 |

In Hexane ($S_0 = 1·48795$).

| A . | S_1 . | v . |
|-------|---------|-------|
| 4·371 | 1·44605 | 0·502 |

*In isoAmyl Acetate
($S_0 = 1·15998$).*

| A . | S_1 . | v . |
|-------|---------|-------|
| 8·648 | 1·10879 | 0·510 |

It will be seen from the above tables that the specific volume (v) of the dibromobenzene remains constant (within the errors of experiment) for any one solvent with the exception of acetic ester and ethyl ether,

with which it increases with increase of the concentration. The nature of the solvent in the other cases has a distinct effect on the value of v , varying from 0.495 in ethyl bromide to 0.513 in benzene, or about 3.5 per cent.

The Specific Volume of Diphenyl in Various Solvents at 25°C.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 2.003 | 1.14155 | 0.970 | 2.699 | 1.15570 | 0.961 |
| 5.492 | 1.13588 | 0.970 | 4.515 | 1.15238 | 0.962 |
| 10.736 | 1.12767 | 0.967 | 9.814 | 1.14291 | 0.956 |
| 14.876 | 1.12175 | 0.965 | 13.543 | 1.13751 | 0.964 |
| 18.118 | 1.11738 | 0.965 | 31.867 | 1.11279 | 0.962 |

| <i>In Acetic Ester.</i> | | | <i>In Chloroform.</i> | | |
|-------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 2.000 | 1.11459 | 0.947 | 1.054 | 0.88131 | 0.947 |
| 4.908 | 1.11009 | 0.950 | 4.375 | 0.88859 | 0.956 |
| 9.147 | 1.10369 | 0.947 | 5.616 | 0.89204 | 0.962 |
| 11.558 | 1.10095 | 0.953 | 11.457 | 0.70635 | 0.944 |
| 20.764 | 1.08902 | 0.949 | 15.136 | 0.71490 | 0.966 |

| <i>In Hexane.</i> | | | <i>In isoAmyl Acetate.</i> | | |
|-------------------|-----------------------|-----------|----------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 2.121 | 1.47639 | 0.931 | 7.467 | 1.14579 | 0.956 |
| 6.877 | 1.45240 | 0.935 | 12.911 | 1.13672 | 0.954 |

| <i>In Nitrobenzene (<i>S₀</i> = 0.8350).</i> | | | <i>In Carbon Disulphide.</i> | | |
|---|-----------------------|-----------|------------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 1.934 | 0.83760 | 0.967 | 3.953 | 0.80315 | 0.974 |
| 4.433 | 0.84103 | 0.975 | 13.253 | 0.81753 | 0.977 |

In Ethyl Ether.

| <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
|-----------|-----------------------|-----------|
| 2.160 | 1.40152 | 0.900 |
| 3.788 | 1.39356 | 0.898 |
| 8.761 | 1.37057 | 0.894 |
| 12.617 | 1.35310 | 0.891 |

It will be noticed in the case of diphenyl that variations from constancy of the value of v are more marked than in the previous case. In benzene v decreases slightly with increase of concentration, whilst in chloroform the opposite is the case. As before, the values in ether are much lower than in any of the other solvents, and a slight fall of v occurs with increase of the concentration. The values in carbon disulphide and nitrobenzene are much greater than the average. The percentage difference between the highest (0.977) and the lowest (0.891) is about 9.

The Specific Volume of Acenaphthene on Various Solvents at 25.00°.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 1.401 | 1.14054 | 0.907 | 2.143 | 1.15572 | 0.911 |
| 4.795 | 1.13456 | 0.913 | 5.644 | 1.14753 | 0.909 |
| 8.490 | 1.12674 | 0.912 | 10.183 | 1.13781 | 0.911 |
| 12.279 | 1.11610 | 0.915 | 21.108 | 1.11756 | 0.912 |

| <i>In Acetic Ester.</i> | | | <i>In Chloroform.</i> | | |
|-------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 3.769 | 1.10984 | 0.895 | 1.515 | 0.68064 | 0.931 |
| 7.922 | 1.10324 | 0.894 | 4.131 | 0.68645 | 0.919 |
| 12.216 | 1.09422 | 0.900 | 7.963 | 0.69461 | 0.918 |
| | | | 15.207 | 0.70920 | 0.922 |

| <i>In Hexane.</i> | | | <i>In Nitrobenzene.</i> | | |
|-------------------|-----------------------|-----------|-------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 3.255 | 1.46880 | 0.871 | 2.915 | 0.83763 | 0.924 |
| 4.945 | 1.45910 | 0.875 | 4.020 | 0.83858 | 0.925 |

| <i>In Ethyl Ether.</i> | | | | | |
|------------------------|-----------------------|-----------|--|--|--|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | | | |
| 3.962 | 1.39015 | 0.829 | | | |
| 6.829 | 1.37509 | 0.829 | | | |
| 8.083 | 1.36922 | 0.835 | | | |

As in the previous cases, low values of *v* for acenaphthene are shown in ethyl ether and hexane, and high values in nitrobenzene. The value increases with the concentration in acetic ester. The value 0.931 in chloroform is very probably too high.

The Specific Volume of Benzil in Various Solvents.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 1.631 | 1.13942 | 0.850 | 2.863 | 1.15225 | 0.848 |
| 6.030 | 1.12808 | 0.848 | 4.358 | 1.14773 | 0.846 |
| 6.324 | 1.12752 | 0.851 | 7.183 | 1.13968 | 0.844 |
| 12.962 | 1.10903 | 0.851 | 20.401 | 1.10818 | 0.850 |
| 23.563 | 1.09488 | 0.851 | 28.260 | 1.09264 | 0.851 |

| <i>In Acetic Ester.</i> | | | <i>In Chloroform.</i> | | |
|-------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_p.</i> | <i>v.</i> | <i>A.</i> | <i>S_p.</i> | <i>v.</i> |
| 2.624 | 1.11221 | 0.830 | 2.074 | 0.68013 | 0.843 |
| 1.911 | 1.10601 | 0.835 | 3.975 | 0.68315 | 0.842 |
| 7.517 | 1.09810 | 0.834 | 10.508 | 0.69290 | 0.846 |
| 17.820 | 1.07552 | 0.837 | 18.093 | 0.70349 | 0.851 |

The Specific Volume of Benzil in Various Solvents—(continued).

| <i>In Nitrobenzene.</i> | | | <i>In Ethyl Ether.</i> | | |
|-------------------------|-----------------------|-----------|------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.836 | 0.83570 | 0.868 | 2.145 | 1.39009 | 0.777 |
| 4.869 | 0.83662 | 0.868 | 5.062 | 1.38164 | 0.772 |
| | | | 11.723 | 1.34574 | 0.774 |

The value of *v* in toluene shows irregularities at small concentrations, but assumes a value identical with that in benzene at higher concentrations. In acetic ester there is a consistent increase with increase of concentration. Again, in nitrobenzene the values are highest, and lowest in ether.

The Specific Volume of Azobenzene in Various Solvents at 25.00°.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.984 | 1.14060 | 0.920 | 2.921 | 1.15367 | 0.905 |
| 3.971 | 1.13625 | 0.916 | 4.670 | 1.14985 | 0.902 |
| 7.866 | 1.12867 | 0.921 | 9.346 | 1.13074 | 0.911 |
| 15.799 | 1.11421 | 0.919 | 12.006 | 1.13471 | 0.909 |

| <i>In Acetic Acid.</i> | | | <i>In Chloroform.</i> | | |
|------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 2.013 | 1.11364 | 0.900 | 3.216 | 0.68410 | 0.979 |
| 4.873 | 1.10777 | 0.899 | 8.087 | 0.69152 | 0.972 |
| 11.757 | 1.09527 | 0.902 | 12.113 | 0.70293 | 0.975 |
| 14.204 | 1.09106 | 0.902 | | | |

| <i>In Ethyl Ether.</i> | | | <i>In Carbon Disulphide.</i> | | |
|------------------------|-----------------------|-----------|------------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 2.055 | 1.40123 | 0.860 | 1.035 | 0.79763 | 0.977 |
| 6.192 | 1.37957 | 0.850 | 6.670 | 0.80475 | 0.974 |
| 9.326 | 1.36859 | 0.841 | 16.442 | 0.81339 | 0.964 |
| 19.892 | 1.31929 | 0.851 | | | |

| <i>In Hexane.</i> | | | <i>In Nitrobenzene.</i> | | |
|-------------------|-----------------------|-----------|-------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.405 | 1.47974 | 0.895 | 1.879 | 0.83689 | 0.942 |
| 3.611 | 1.46632 | 0.899 | 4.689 | 0.83939 | 0.942 |

The Specific Volume of Durene in Various Solvents at 25.00°.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 2.663 | 1.14555 | 1.167 | 3.032 | 1.18033 | 1.157 |
| 7.571 | 1.14591 | 1.159 | 7.262 | 1.16013 | 1.149 |
| 10.572 | 1.14636 | 1.159 | 7.080 | 1.15992 | 1.145 |
| 15.757 | 1.14609 | 1.158 | 19.621 | 1.15758 | 1.140 |
| 18.951 | 1.14624 | 1.154 | | | |
| 30.322 | 1.14657 | 1.159 | | | |

| <i>In Acetic Ester.</i> | | | <i>In Chloroform.</i> | | |
|-------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.144 | 1.11798 | 1.122 | 1.983 | 0.68636 | 1.168 |
| 3.039 | 1.11882 | 1.147 | 4.876 | 0.69941 | 1.163 |
| 9.169 | 1.12005 | 1.132 | 11.286 | 0.72558 | 1.157 |
| 14.326 | 1.12105 | 1.143 | 16.167 | 0.74363 | 1.150 |

| <i>In Hexane.</i> | | | <i>In Nitrobenzene.</i> | | |
|-------------------|-----------------------|-----------|-------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 2.652 | 1.47838 | 1.114 | 2.058 | 0.84091 | 1.125 |
| 10.903 | 1.45203 | 1.123 | 6.129 | 0.85196 | 1.127 |
| 16.115 | 1.45099 | 1.222 | | | |

It will be noticed that in most cases the value of *v* changes with the concentration. Notice the abnormally low values in nitrobenzene and comparatively high values in hexane as compared with the values in solvents in the other cases.

The Specific Volume of Triphenylmethane in Various Solvents at 25.00°.

| <i>In Benzene.</i> | | | <i>In Toluene.</i> | | |
|--------------------|-----------------------|-----------|--------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.577 | 1.14140 | 0.930 | 4.007 | 1.15131 | 0.916 |
| 2.565 | 1.13929 | 0.927 | 7.976 | 1.14335 | 0.922 |
| 7.290 | 1.13010 | 0.926 | 12.558 | 1.13458 | 0.917 |
| | | | 21.781 | 1.11315 | 0.921 |

| <i>In Acetic Ester.</i> | | | <i>In Chloroform.</i> | | |
|-------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.810 | 1.11403 | 0.900 | 2.748 | 0.68340 | 0.919 |
| 6.774 | 1.10521 | 0.917 | 7.333 | 0.69273 | 0.923 |
| 10.190 | 1.09913 | 0.919 | 7.561 | 0.69442 | 0.927 |
| | | | 10.138 | 0.69997 | 0.928 |

| <i>In Hexane.</i> | | | <i>In Ethyl Ether.</i> | | |
|-------------------|-----------------------|-----------|------------------------|-----------------------|-----------|
| <i>A.</i> | <i>S_v.</i> | <i>v.</i> | <i>A.</i> | <i>S_v.</i> | <i>v.</i> |
| 1.892 | 1.47690 | 0.893 | 1.571 | 1.40391 | 0.865 |
| 3.105 | 1.46998 | 0.891 | 8.507 | 1.36896 | 0.859 |

The above case is of particular interest, because triphenylmethane crystallises from benzene with one molecule of benzene of crystallisation (Kekulé and Franchimont, *Ber.*, 1872, 5, 967). Moreover, it is probable, although not conclusive, that in solution in benzene a portion at least of the triphenylmethane exists in combination with the benzene. This does not, however, seem to affect at all considerably the value of (v). It is unfortunate that a limiting solubility prevents the extension of the experiments in this case any farther.

It might be stated from a consideration of the above tables, that the specific volume of the solute in a normal solvent is approximately a constant independent of the concentration of the solution, and, with certain limitations, independent of the solvent. Although the term "specific volume of solute in solution" or "specific solution volume" has been used throughout this paper, it is not intended to imply that this represents the actual volume occupied by the solute in the solution, but the term is used from considerations of usage and simplicity. It has been usual with other investigators to express the results in terms of the molecular solution volume, but as no particular advantages appear to accrue from this method, the results here have been left in terms of the specific solution volume.

It has been shown repeatedly in a few cases that the volume of the solute in solution is equal to the volume occupied by the same weight of the solute when in the liquid state at the same temperature (Beilby, *loc. cit.*; Lumsden, *loc. cit.*; Forch, *loc. cit.*; Dawson, this vol., p. 1041). Now if the rule that the specific volume of the solute in solution is independent of the concentration holds to a concentration of 100 per cent. (that is, pure liquid solute)—and it has been shown in the above tables that it holds to comparatively large concentrations—the above observation follows at once.

In spite of a very close agreement between the values of v for a given solute in many of the solvents, there is, however, a distinct difference between the values of v in one solvent from the values in another. If the tables be inspected, it will be noticed that there seems to be some connexion between the nature of the solvent and the variation of the value of the specific solution volume of the solute from a certain mean value. For example, in every case the values in ether are lowest and those in carbon disulphide or nitrobenzene highest. If we arrange the solvents in order of magnitude of the specific solution volume of a solute, we obtain approximately the following sequence in every case except durene: (1) carbon disulphide, (2) nitrobenzene, (3) benzene, (4) toluene, (5) chloroform, (6) acetic ester, (7) benzene, (8) ethyl ether.

On the other hand, Dawson (*loc. cit.*) showed that in the two cases he investigated (iodine and naphthalene) no such similarity in arrange-

ment was observable. The order for naphthalene is, however, very similar to the above. The two cases, iodine and durene, are quite apart, showing an entirely different order of arrangement of solvents. And it will be seen from the table that the specific volume of durene in solution varies also with the concentration, and this is strong evidence that in this case chemical changes occur in the solution, such as association or dissociation, for, in aqueous solutions where these chemical changes are known to take place, similar variations of the volume of the solute are observed.

This, however, will not suffice to explain the influence of the solvent. Let us consider the matter from the point of view of the molecular theory. In the ideal case no change in volume occurs on formation of a solution whatever the nature of the solvent. That is to say, the space taken up by each molecule of the solute is independent of the nature of the surrounding molecules. Now, in virtue of its kinetic energy, each molecule in a liquid exerts a certain pressure, which is proportional to the value of this energy, and depends also on the mean distance between two adjacent molecules. This pressure is counterbalanced by a molecular force of attraction. Therefore if a molecule of a solute, when surrounded by an atmosphere of solvent molecules, is to occupy the same volume as in its own liquid at the same temperature, then the attractive force acting on the molecule must be the same in both cases. If this attractive force is greater, there will ensue a closer grouping of solvent molecules around each molecule of solute (this does not mean that the two necessarily combine), and the observed specific solution volume of the solute will be diminished. This attractive force is identical with the force which undoubtedly plays a part in the dissolution of a solute, and, to some extent, the solubility (if small) might be regarded as a measure of this attractive force, but other factors come into consideration complicating the matter (see this vol., p. 1778).

In the contraction or expansion of the solvent its compressibility must be taken into consideration. The extent of this contraction or expansion will depend on two factors, namely: (1) the force of attraction between the molecule of solute and the surrounding solvent molecules; (2) the pressure or force necessary to bring about a very small change in the mean distance between the molecules of the solvent. The latter factor is the more important, and is approximately proportional to the product of the compressibility, β , and the molecular volume, V . If we arrange the solvents used in the above experiments in order of the values of βV , we get approximately the following sequence: (1) carbon disulphide, (2) benzene, (3) toluene, (4) chloroform, (5) ethyl acetate, (6) hexane, (7) ethyl ether.

This is exactly the same order of arrangement as given above for

the variation of the specific volume of a solute. This is strong evidence in favour of the view that a connexion exists between the compressibility of a solvent and the volume which a solute, when dissolved in it, takes up. There is, however, the other factor to be considered. It is probable that with substances of nearly equal molecular solubility, this factor is constant, but at this stage of the subject there is not sufficient experimental data to make a systematic examination of the hypothesis.

In the ideal case when the attraction of the molecules of the solvent for a molecule of a dissolved solute is equal to the attraction exerted on the molecule when present in the pure liquid solute at the same temperature, the volume change occurring on the formation of the solution will be due entirely to the solute, and the property will be strictly additive.

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CCLXIX.—*Studies of Dynamic Isomerism. Part XII.*
The Equations for Two Consecutive Unimolecular Changes.

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B.A., B.Sc.

THE problem considered in the following pages is to determine the course of a chemical change which proceeds in two stages, each reversible and each obeying the unimolecular law. Two cases are considered:

- (1) That in which the total quantity of material is constant, as is usually the case when isomeric changes are studied in solution.
- (2) That in which the concentration of one of the constituents is kept constant, as, for instance, when isomeric change takes place in a solution saturated with one of the isomerides.

Work in this direction has already been done by Harcourt and Esson (*Phil. Trans.*, 1866, 156, 193) and by Mellor (*Chemical Statics and Dynamics*, Chapter V), who has given the equations for two consecutive non-reversible actions: $X \rightarrow Y \rightarrow Z$ (*loc. cit.*, pp. 98, 114), and has calculated the course of the action in one particular case. P. V. Bevan (*Phil. Trans.*, 1904, A. 202, 71) has given the equations and has calculated one series of values for the case $X \rightleftharpoons Y \rightarrow Z$.

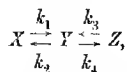
Finally, Rakowski (*Zeitsch. physikal. Chem.*, 1906, 57, 321) has investigated the general case of n consecutive unimolecular actions, and has plotted series of curves for the special cases $X \rightarrow Y \rightarrow Z^*$ and $X \rightarrow Y \rightleftharpoons Z$. General equations for the case $X \rightleftharpoons Y \rightleftharpoons Z$ were given by Rakowski, but no further investigation was made.

The inquiry, of which the results are now described, was begun in 1903, at which date the majority of the solutions referred to above were not available. It was hoped that the study of the equations for the action $X \rightleftharpoons Y \rightleftharpoons Z$ might throw light on the question of the existence in aqueous solutions of dextrose of a substance intermediate between α - and β -glucose (compare *Trans.*, 1903, 83, 1314). At the request of one of us, the equations shown on p. 2612 were then worked out by Mr. H. Klugh, of the Central Technical College, for the case in which the concentration of one of the constituents is kept constant by contact with the solid. This case, so far as we are aware, has not been considered by any other investigator. The comparison of theory and experiment presented, in the case of the sugars, difficulties which were sufficiently great to prevent the utilisation at the time of the information which had been obtained; but the recent discovery of a series of inflected mutarotation curves rendered urgent the study of the commoner case in which the sum of the concentrations is constant, and led to the detailed inquiry recorded below.

Previous investigators have shown that under certain conditions the intermediate substance Y increases to a maximum concentration and then decreases again, whilst the concentration of the final product Z gives rise to an inflected curve when plotted against t . Our own inquiry has included the study of the intermediate substance, but special attention has been paid to the inflected curves for the final product, and a method has been devised whereby these curves may be characterised readily by drawing or calculating the intercepts of the stationary tangent on the lines which indicate the initial and final concentrations of the product.

General Solution. Case I.

If the concentrations of the three substances X , Y , and Z be represented by x , y , and z , and the four velocity constants by k_1 , k_2 , k_3 , k_4 , as shown in the scheme :



* Compare Walker, *Zeitsch. physikal. Chem.*, 1899, 28, 177.

the fundamental equations are:

$$\frac{dx}{dt} = -k_1x + k_2y$$

$$\frac{dy}{dt} = +k_1x - (k_2 + k_4)y + k_3z$$

$$\frac{dz}{dt} = -k_3z + k_4y.$$

In the case of unsaturated solutions in which the total concentration is constant: $x + y + z = \text{const.} = 1$, the constant being taken as unity in order to simplify the algebraical working. The assumption has also been made that the experiments are carried out with materials initially homogeneous, so that when $t=0$, $x=1$, $y=0$, $z=0$, and in addition $dz/dt=0$.

The solution of the differential equations is as follows:

$$\begin{aligned} x &= x_\infty \left\{ -\frac{m_2}{m_2 - m_1} e^{-m_1 t} + \frac{m_1}{m_2 - m_1} e^{-m_2 t} + 1 \right\} + \frac{m_2 - k_1}{m_2 - m_1} e^{-m_1 t} + \frac{k_1 - m_1}{m_2 - m_1} e^{-m_2 t} \\ y &= y_\infty \left\{ -\frac{m_2}{m_2 - m_1} e^{-m_1 t} + \frac{m_1}{m_2 - m_1} e^{-m_2 t} + 1 \right\} + \frac{k_1}{m_2 - m_1} \left\{ e^{-m_1 t} - e^{-m_2 t} \right\} \\ &= y_\infty \left\{ -\frac{m_2(k_2 - m_1)}{k_3(m_2 - m_1)} e^{-m_1 t} + \frac{m_1(k_2 - m_2)}{k_3(m_2 - m_1)} e^{-m_2 t} + 1 \right\} \\ z &= z_\infty \left\{ -\frac{m_2}{m_2 - m_1} e^{-m_1 t} + \frac{m_1}{m_2 - m_1} e^{-m_2 t} + 1 \right\} \end{aligned}$$

where:

$$x_\infty = \frac{k_2 k_3}{k_2 k_3 + k_1 k_3 + k_1 k_4}$$

$$y_\infty = \frac{k_1 k_3}{k_2 k_3 + k_1 k_3 + k_1 k_4}$$

$$z_\infty = \frac{k_1 k_4}{k_2 k_3 + k_1 k_3 + k_1 k_4}$$

$$m_1 = \frac{1}{2} \{ (k_1 + k_2 + k_3 + k_4) - \sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2 k_3 + k_1 k_3 + k_1 k_4)} \}$$

$$m_2 = \frac{1}{2} \{ (k_1 + k_2 + k_3 + k_4) + \sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2 k_3 + k_1 k_3 + k_1 k_4)} \}$$

$$m_1 m_2 = k_2 k_3 + k_1 k_3 + k_1 k_4.$$

These functions undergo a remarkable simplification when one or more of the velocity constants is reduced to zero. Thus, if the first stage of the action is non-reversible, $k_2=0$, and the m functions are reduced to the simple form:

$$m_1 = k_1; \quad m_2 = k_3 + k_4;$$

if the second stage of the action is non-reversible, $k_4=0$, and

$$m_1 = k_1 + k_2; \quad m_2 = k_3;$$

if both stages are non-reversible, $k_2=k_4=0$, and

$$m_1 = k_1; \quad m_2 = k_3,$$

or vice versa.

Under these conditions, the original equations can be given in terms of the velocity constants without making use of m_1 and m_2 . But the simplified equations, as investigated by Mellor, by Bevan, and by Rikowski, are of very little value in the study of dynamic isomerism, since they can only be applied to non-reversible isomeric changes, and are inapplicable in all those cases in which the original substance can be recovered from its solutions by recrystallisation. We have therefore been obliged to devote our attention to discovering exactly how much information can be obtained from the study of the experimental curves in the general case in which both actions are reversible and all the constants are finite and unknown.

Form of the yt Curves. Case I.

The chief feature of the yt curves is the occurrence under some conditions of a maximum concentration, followed by a decrease to the limiting value y_∞ . The condition $dy/dt=0$ gives for the co-ordinates of the maximum the values:

$$t_m = \frac{1}{m_2 - m_1} \log e \frac{m_2 - k_3}{m_1 - k_3},$$

$$\frac{y_m}{y_\infty} = 1 + \frac{m_2 - k_3}{k_3} \left(\frac{m_2 - k_3}{m_1 - k_3} \right)^{-\frac{m_2}{m_2 - m_1}}.$$

If k_3 lies between m_1 and m_2 , the ratio $\frac{m_2 - k_3}{m_1 - k_3}$ is negative and the logarithm imaginary; the yt curve then runs up steadily from the origin to the limiting value without passing through an intermediate maximum.

A maximum would occur if k_3 were greater than m_2 or less than m_1 . The former condition we have proved to be impossible. As regards the relative magnitudes of k_3 and m_1 , we have found that when k_3 is equal to m_1 , $k_3 = m_1$, whilst $k_3 > m_1$ gives $k_3 > k_1$. The occurrence of a maximum in the yt curve thus depends only on the relative magnitude of k_3 and k_1 ; if $k_3 > k_1$, no maximum can be developed whatever values are assigned to k_3 and k_1 , whilst if $k_3 < k_1$, a maximum always appears.

It is noteworthy that when $k_3 = k_1$, the $e^{-m_1 t}$ factor of the yt equation vanishes and the curve assumes the simple logarithmic form characteristic of a single unimolecular action.

The dependence of the form of the yt curve on the constants k_1 and k_2 , and the small influence of the constants k_3 and k_4 , naturally extend to the simpler cases in which k_2 or $k_4 = 0$; they were pointed out by Rikowski as applying under these conditions, but the general case had not been investigated previously.

the presence of a catalyst or impurity, and proceed with different velocities in the case of samples of different degrees of purity. These features are the co-ordinate z_i of the point of inflexion, especially when expressed by the ratio z_i/z_∞ and the ratio t_a/t_b of the intercepts t_a and t_b of the stationary tangent upon the lines $z=0$ and $z=z_\infty$.

The condition $\frac{dz_\infty}{dt^2}=0$ gives for the point of inflexion the co-ordinates:

$$t_i = -\frac{1}{m_2 - m_1} \log_e \frac{m_2}{m_1},$$

$$z_i = -\frac{m_2}{m_2 - m_1} \left(\frac{m_2}{m_1}\right)^{-\frac{m_1}{m_2 - m_1}} + \frac{m_1}{m_2 - m_1} \left(\frac{m_2}{m_1}\right)^{-\frac{m_2}{m_2 - m_1}} + 1$$

$$= 1 - \frac{m_2 + m_1}{m_1} \left(\frac{m_2}{m_1}\right)^{-\frac{m_2}{m_2 - m_1}}.$$

Unlike the co-ordinates for the maximum in the yt curve, these expressions are always real, and the point of inflexion is a regular feature of all the zt curves.

The tangent at the point of inflexion is given by the equation:

$$z - z_i = m(t - t_i),$$

where

$$m = z_\infty \frac{m_1 m_2}{m_2 - m_1} \{e^{-m_1 t_i} - e^{-m_2 t_i}\}$$

$$= z_\infty m_2 \left(\frac{m_2}{m_1}\right)^{-\frac{m_2}{m_2 - m_1}}.$$

The intercepts, obtained by substituting $z=0$ and $z=z_\infty$ in the above equation, are given by

$$t_a = t_i - z_i/m$$

$$t_b = t_i + (z_\infty - z_i)/m.$$

The intercept-ratio is then found by substitution to be

$$\frac{t_a}{t_b} = 1 - \left(\frac{m_2}{m_1}\right)^{-\frac{m_1}{m_2 - m_1}} / \left\{ -\frac{m_2}{m_2 - m_1} \log_e \frac{m_2}{m_1} + \frac{m_2 + m_1}{m_1} \right\}.$$

It will be noticed that the ratios z_i/z_∞ and t_a/t_b depend directly on the ratio m_2/m_1 , but that none of the individual velocity constants are present in the formulæ by which the values of these ratios are determined. The experimental study of the zt curves can therefore be used to determine the ratio m_2/m_1 , but is only indirectly of value in determining the magnitudes of the individual velocity constants. The expressions which give the ratios z_i/z_∞ and t_a/t_b in terms of m_1 and m_2 are too complex to be solved easily, even when the numerical values of these ratios are known; we have therefore calculated the following table, from which the values of m_2/m_1 corresponding with any given values of z_i/z_∞ and t_a/t_b may be determined by interpolation:

TABLE I.

| m_2/m_1 or m_4/m_3 | z_i/z_∞ | t_a/t_b |
|------------------------|----------------|-----------|
| 6.0 | 0.185 | 0.0607 |
| 5.0 | 0.198 | 0.0667 |
| 4.0 | 0.213 | 0.0720 |
| 3.0 | 0.230 | 0.0800 |
| 2.5 | 0.240 | 0.0841 |
| 2.0 | 0.250 | 0.0881 |
| 1.4 | 0.261 | 0.0924 |
| 1.2 | 0.263 | 0.0931 |
| 1.1 | 0.264 | 0.0938 |
| 1.0 | 0.264 | 0.0939 |

The limiting values, when $m_2/m_1 = 1$, are

$$\frac{z_i}{z_\infty} = 1 - \frac{2}{e} = 0.264,$$

$$\frac{t_a}{t_b} = 1 - \frac{e}{3} = 0.0939;$$

it follows, therefore, that if an experimental curve gives values in excess of these figures it cannot be due to two successive unimolecular changes, but probably depends on some more complex sequence.

Having determined the ratio m_2/m_1 from the ratios z_i/z_∞ and t_a/t_b , it would be easy to deduce from $t_i = \frac{1}{m_2 - m_1} \log_e \frac{m_2}{m_1}$ the individual values of m_2 and m_1 , but these would probably be found to vary widely according to the amount of catalyst or impurity present in the experimental material; it is for this reason that we have laid special emphasis on determining the ratio m_2/m_1 and the ratios $k_1:k_2:k_3:k_4$, rather than the absolute values of these quantities. As a trace of catalyst cannot alter the character of the final equilibrium, the ratios k_2/k_3 and k_3/k_4 must be independent of the speed of the action; a similar statement would probably be true of the ratios $k_1/k_2:k_3/k_4$ and m_2/m_1 if the quantity, and not the nature, of the catalyst were changed, but an alteration in the relative speeds of the two stages of the action might be produced if a different catalyst were introduced into the system.

Transposition of Constants. Case I.

On examining the equations given above, it will be seen that the equations connecting z and t , as well as the equations for the co-ordinates of the point of inflexion and for the stationary tangent, do not contain any of the individual velocity constants, except in so far as these serve to determine the values of m_1 , m_2 , and z_∞ . It therefore follows that when z/z_∞ is plotted against t , the course of the curve is determined entirely and exclusively by the values of m_1 and m_2 . From this fact some important conclusions may be drawn.

1. The m functions are symmetrical in reference to k_1k_2 and k_3k_4 . It is therefore possible to interchange k_1 and k_2 with k_3 and k_4 without altering in the slightest the course of the zt curve. Thus:

(a) On comparing the three equilibria

$$1 \frac{2}{2} 1 \frac{1}{1} 1 \quad 1 \frac{1}{1} 1 \frac{1}{1} 1 \quad 1 \frac{1}{1} 1 \frac{2}{2} 1^*,$$

in which the final proportions are the same throughout, but the relative velocity of the two changes is altered, it is noteworthy that the first and third give identical curves for z and t , although these differ widely from the curve for the second equilibrium; the three yt curves (which involve k_1) are also entirely different from one another.

(b) In the case of the equilibria:

$$\begin{array}{cc} 2 \frac{1}{2} 1 \frac{1}{1} 1 & 1 \frac{1}{1} 1 \frac{1}{2} 2 \\ 1 \frac{2}{1} 2 \frac{1}{1} 2 & 2 \frac{1}{1} 2 \frac{2}{1} 1 \\ 1 \frac{2}{1} 2 \frac{1}{2} 4 & 4 \frac{1}{2} 2 \frac{2}{1} 1 \end{array}$$

the form of the curve obtained by plotting z/z_∞ against t is in every respect precisely the same for the two members of each pair, in spite of the alterations which are produced in the values of z_∞ by the transposition of the constants. It is a noteworthy contrast that the alteration of relative velocities on passing from

$$2 \frac{1}{2} 1 \frac{1}{1} 1 \text{ to } 2 \frac{1}{2} 1 \frac{1}{1} 1$$

alters completely the form of the zt curve, in spite of the fact that the ultimate proportions of the three isomerides remain unchanged.

2. If $k_1=k_3$ the m functions contain the other two velocity constants only in the form k_2+k_4 . It is therefore possible to increase k_2 at the expense of k_4 , or vice versa, without affecting in the slightest the form of the curve for z/z_∞ against t . Identical curves are therefore given by the equilibria:

$$3 \frac{2}{3} 2 \frac{2}{1} 1 \quad 2 \frac{2}{2} 2 \frac{2}{2} 2 \quad 1 \frac{2}{1} 2 \frac{2}{3} 3 \quad 0 \frac{2}{0} 2 \frac{2}{4} 4,$$

in which the equilibrium is gradually displaced in favour of Z at the expense of X , until X disappears altogether, owing to the non-reversibility of the change $X \rightarrow Y$.

Even more remarkable is the fact that when $k_1=k_3$, the above transformation can be made without affecting the form of yt curve, which remains unaltered (for instance) over the whole range from

$$4 \frac{2}{4} 2 \frac{2}{0} 0 \quad \text{to} \quad 0 \frac{2}{0} 2 \frac{2}{2} 4.$$

* The final proportions of x , y , and z are here shown by simple integers, for example, 1:1:1, instead of the actual values, 0.33:0.33:0.33 of $x_\infty : y_\infty : z_\infty$.

In the former limiting case the third isomeride Z is not formed at all since $k_1 = 0$; the yt curve has therefore the simple unimolecular form, and this form is retained throughout the whole series of equilibria. It is noteworthy that the above transformation leaves the yt curves unaltered, and not merely the curves for y/y_∞ against t , y/z (unlike z/z_∞) remaining constant in value throughout.

General Solution. Case II.

The fundamental equations for a saturated solution in which the concentration of the original substance is kept constant by contact with the solid are:

$$\begin{aligned} x = 1 \quad \frac{dy}{dt} &= k_1 - (k_2 + k_4)y + k_3z \\ \frac{dz}{dt} &= k_3y - k_3z, \end{aligned}$$

the initial concentration being taken again as unity in order to simplify the algebraical working.

The general solution is:

$$\begin{aligned} x = 1 \quad y &= y_\infty \left\{ -\frac{m_4 - k_2 e^{-m_3 t}}{m_4 - m_3} - \frac{k_2 - m_3 e^{-m_4 t}}{m_4 - m_3} + 1 \right\} \\ z &= z_\infty \left\{ -\frac{m_4}{m_4 - m_3} e^{-m_3 t} + \frac{m_3}{m_4 - m_3} e^{-m_4 t} + 1 \right\} \end{aligned}$$

where

$$\begin{aligned} y_\infty &= \frac{k_1}{k_2}; \quad z_\infty = \frac{k_1 k_4}{k_2 k_3}, \\ m_3 &= \frac{1}{2}[(k_2 + k_3 + k_4) - \sqrt{(k_2 + k_3 + k_4)^2 - 4k_2 k_3}], \\ m_4 &= \frac{1}{2}[(k_2 + k_3 + k_4) + \sqrt{(k_2 + k_3 + k_4)^2 - 4k_2 k_3}], \\ m_3 m_4 &= k_2 k_3. \end{aligned}$$

Form of the Curves. Case II.

The condition, $dy/dt = 0$, for a maximum in the yt curve leads in this case to the equation:

$$t_{\max.} = -\frac{1}{m_2 - m_1} \log_e \frac{k_2 - m_4}{k_2 - m_3}$$

The logarithm is imaginary if k_2 lies between m_4 and m_3 . This we find, must always be the case: the development of a maximum in the yt curve is therefore impossible, whatever values may be assigned to the velocity constants.

The equation for the zt curve is remarkable in that it has precisely the same form as in Case I, the only difference being that the limiting value, z_∞ , and the m functions, m_3 and m_4 , are derived in a different way from the velocity constants k_1 , k_2 , k_3 , and k_4 . The difference can be expressed very simply by taking the expressions for the unsaturated solution of Case I and making $k_1 = 0$ in order to convert m_1 and m_2 into m_3 and m_4 , but this transformation has no experimental significance, as

κ_1 appears in the expression for z_∞ . It is, however, important to notice that the ratio m_1/m_2 may be determined from the experimental values of τ , τ_∞ and t_a/t_b for a saturated solution by the same equations and formulae that were used to deduce m_2/m_1 in the case of an unsaturated solution, the table on p. 2640 being equally applicable in either case. The alteration in the form of the m functions has the effect of rendering them unsymmetrical in reference to k_1 and k_2 and k_3 and k_4 ; as a consequence of this alteration an interchange in the relative velocities of the two stages of the action cannot be made without altering the form of the zt curve.

Transposition of Constants. Case II.

The most important transformations in Case II are as follows:

1. The m functions do not contain k_1 ; moreover, this constant enters into the equations for yt and zt only as determining the values of y_∞ and z_∞ . The curves for y/y_∞ against t , and for z/z_∞ against t , are therefore entirely independent of k_1 . Identical curves are thus given by the equilibria:

$$2 \frac{\frac{1}{2}}{\frac{1}{2}} 1 \frac{1}{1} 1 \qquad 1 \frac{1}{1} 1 \frac{1}{1} 1 \qquad \frac{1}{2} \frac{2}{1} 1 \frac{1}{1} 1,$$

and so on, up to the limiting case when k_1 has a very high value and the action becomes non-reversible.

2. The m functions are symmetrical in reference to k_3 and k_4 . These constants can therefore be interchanged without affecting the form of the zt curves, the value of z_∞ being unaffected by the transposition. Identical zt curves are therefore given by the four equilibria:

$$2 \frac{1}{2} 1 \frac{1}{1} 1 \qquad 2 \frac{1}{1} 2 \frac{2}{1} 1 \qquad 1 \frac{2}{2} 1 \frac{1}{1} 1 \qquad 1 \frac{2}{1} 2 \frac{2}{1} 1,$$

the identity of the first pair with the second pair being established by means of the first transformation. This second transformation cannot be effected in the case of the yt curves, which depend in a special way on the value of k_2 .

Numerical Values.

In order to illustrate the form of the curves, values have been worked out for y and z against t in the case of the three equilibria:

$$1 \frac{2}{2} 1 \frac{1}{1} 1 \qquad 1 \frac{1}{1} 1 \frac{1}{1} 1 \qquad 1 \frac{1}{1} 1 \frac{2}{2} 1$$

both for unsaturated solutions ($x+y+z=1$) and for saturated solutions ($x=1$). It will be noticed that the final equilibrium is the same throughout, but that there is an increase in the velocity of the first or of the second stage of the action in the first and last cases.

Case I.—In considering the unsaturated solutions one of the most notable features is the maximum in the yt curve when the velocity

constants are 2211, the first stage proceeding twice as rapidly as the second. When the two stages are equally rapid, the curve, for constants 1111, is of the simple unimolecular type. When the constants are 1122, the growth of y is choked by the increased velocity with which it passes into z , and the curve falls below the preceding one of unimolecular type. The zt curves show the usual "period of induction" or horizontal tangent at the origin, and also exhibit points of inflexion; it is noteworthy that the curve becomes more inflected if the two stages are made to proceed with unequal velocities, but that identical effects are produced by accelerating either the first or the second stage of the action; doubling the velocity of either stage raises the point of inflexion from 21.7 to 23.0 per cent. of the final value, and increases the ratio of the intercepts of the stationary tangent from 0.075 to 0.080.

Case II.—The six curves that are plotted for saturated solution call for but little comment. Two of the yt curves, those for constants 1111 and 1122, intersect at $t=3$ (approx.), in addition to being coincident at the origin, $t=0$, and at $t=\infty$. The zt curves are all distinct, the inflected character of the curve being increased by accelerating the first, and decreased by accelerating the second, stage of the action, the ordinate of the point of inflexion being changed from 0.175 to 0.187 and 0.146 respectively, whilst the intercept ratio, 0.058, is increased to 0.062 in the former, and decreased to 0.045 in the latter, case.

TABLE II. Numerical Values.

| t | Case I. | | | | Case II. | | | |
|--|----------------|-------|----------------|-------|----------------|-------|----------------|-------------|
| | y/y_{∞} | | z/z_{∞} | | y/y_{∞} | | z/z_{∞} | |
| | 2211. | 1111. | 1122. | 2211. | 1111. | 1122. | 2211. | 1111. 1122. |
| 0.1 | 0.471 | 0.259 | 0.248 | 0.025 | 0.013 | 0.173 | 0.091 | 0.087 |
| 0.2 | 0.753 | 0.451 | 0.418 | 0.082 | 0.046 | 0.303 | 0.166 | 0.154 |
| 0.4 | 1.014 | 0.690 | 0.621 | 0.232 | 0.155 | 0.478 | 0.282 | 0.254 |
| 0.6 | 1.091 | 0.835 | 0.737 | 0.383 | 0.260 | 0.584 | 0.367 | 0.328 |
| 0.8 | 1.102 | 0.909 | 0.807 | 0.512 | 0.358 | 0.654 | 0.433 | 0.383 |
| 1.0 | 1.091 | 0.950 | 0.855 | 0.619 | 0.473 | 0.705 | 0.488 | 0.441 |
| 1.2 | 1.075 | 0.973 | 0.889 | 0.703 | 0.562 | 0.744 | 0.531 | 0.489 |
| 1.4 | 1.060 | 0.985 | 0.915 | 0.769 | 0.638 | 0.776 | 0.569 | 0.532 |
| 1.6 | 1.047 | 0.992 | 0.934 | 0.821 | 0.701 | 0.802 | 0.603 | 0.572 |
| 1.8 | 1.037 | 0.995 | 0.949 | 0.861 | 0.751 | 0.825 | 0.634 | 0.608 |
| 2.0 | 1.029 | 0.998 | 0.960 | 0.892 | 0.798 | 0.845 | 0.662 | 0.641 |
| 2.5 | 1.015 | 0.999 | 0.979 | 0.943 | 0.877 | 0.884 | 0.726 | 0.711 |
| 3.0 | 1.008 | 1.000 | 0.989 | 0.970 | 0.925 | 0.914 | 0.770 | 0.768 |
| 4.0 | 1.002 | — | 0.997 | 0.991 | 0.972 | 0.952 | 0.843 | 0.850 |
| 5.0 | 1.001 | — | 0.999 | 0.998 | 0.990 | 0.973 | 0.893 | 0.904 |
| 10.0 | 1.000 | — | 1.000 | 1.000 | 1.000 | 0.999 | 0.984 | 0.990 |
| t_m or t_i | 0.778 | No | No | 0.549 | 0.380 | No | No | No |
| $\frac{y_m}{y_{\infty}}$ or $\frac{z_i}{z_{\infty}}$ | 1.102 | max. | max. | 0.230 | 0.217 | max. | max. | max. |
| t_m | — | — | — | 0.151 | 0.103 | — | — | — |
| t_b | — | — | — | 1.853 | 1.380 | — | — | — |
| t_m/b | — | — | — | 0.080 | 0.075 | — | — | — |

Summary and Conclusions.

1. Equations are given for the changes of concentration which take place in a reversible chemical action which proceeds in two stages, each obeying the unimolecular law. When the total concentration is constant the intermediate form may pass through a maximum concentration, but this is not possible when the concentration of the initial form is kept constant, for instance, by saturation with the solid. In each case, however, the growth of the third form is represented by curves which exhibit a period of induction and a point of inflexion.

2. The occurrence of a maximum concentration of the intermediate form depends exclusively on the velocities with which it is produced from the other two, and is independent of the velocities with which it passes into the final form.

3. The inflected curves showing the growth of the concentration of the final product are independent of the individual velocity constants, except in so far as these determine the value of certain "m" functions, involving in the case of unsaturated solutions all the four velocity constants, but in the case of a saturated solution only three of them. The ratio of the two "m" functions can be deduced from the concentration at which the point of inflexion occurs, or by drawing the stationary tangent and measuring its intercepts on the lines showing the initial and final concentrations of the product. If the concentration at the point of inflexion is greater than 26.4 per cent. of the final concentration, or if the ratio of the intercepts is greater than 0.0939, the curve cannot be due to two consecutive unimolecular actions and must depend on some more complex sequence.

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XLXX.—The Dinitro-derivatives of Dimethyl-p-toluidine

By GILBERT T. MORGAN and ARTHUR CLAYTON.

THE nitration of aromatic amines under various conditions presents certain features of considerable theoretical interest in connexion with the mode in which substitution occurs in the aromatic nucleus.

In many cases it is found desirable to moderate the action of nitric acid on these bases by nitrating them in the form of their acyl derivatives, the acetyl compound being most frequently employed for this purpose. This method of nitration leads, in the great majority of cases, to the production of ortho- and para-nitro-

derivatives, the substitution of the nitro-group in these conditions obeying the ortho-para law.

When, however, the benzenoid amines are nitrated in concentrated sulphuric acid, the nitro-group tends to enter a meta-position with respect to the aminic nitrogen, so that the chief product is frequently, although not invariably, a meta-nitro-derivative in conformity with the meta law of substitution. Aniline, for instance, when nitrated in excess of concentrated sulphuric acid, gives a mixture of nitro-compounds, in which *m*-nitroaniline predominates. *o*-Toluidine, under similar conditions, yields 4-nitro- and 6-nitro-*o*-toluidine, whilst *p*-toluidine furnishes 2-nitro-*p*-toluidine, these three products each having the nitro-group in a meta-position with regard to the aminic nitrogen.

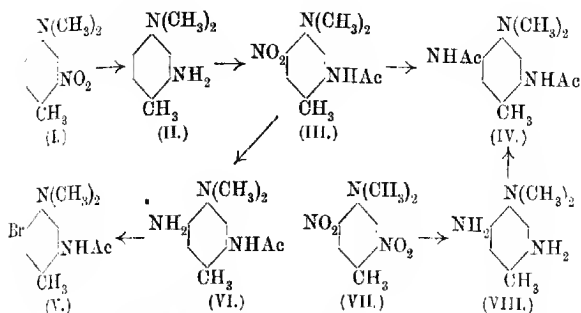
The nitration of the aromatic monoalkyl amines in concentrated sulphuric acid proceeds along similar lines, methyl-*o*-toluidine and methyl-*p*-toluidine yielding respectively 4-nitromethyl-*o*-toluidine and 2-nitromethyl-*p*-toluidine (Gnehm and Blumer, *Annalen*, 1899, **304**, 99; Pinnow, *Ber.*, 1895, **28**, 3040).

The case of the tertiary bases presents several points of interest. Dimethylaniline yields a mixture containing three to four parts of *m*-nitrodimeethylaniline to one part of *p*-nitrodimeethylaniline (Grell, *Ber.*, 1886, **19**, 1944). Dimethyl-*o*-toluidine and dimethyl-*p*-toluidine give rise respectively to 4-nitrodimeethyl-*o*-toluidine and 2-nitrodimeethyl-*p*-toluidine, in both of which the nitro-group is meta to the aminic nitrogen (Gnehm and Blumer, *loc. cit.*, p. 167, and D.R.P. 69188).

When dimethyl-*p*-toluidine, dissolved in concentrated sulphuric acid, is treated with sufficient strong nitric acid to form di- or even tri-nitro-derivatives, the reaction nevertheless proceeds only to the extent of producing 2-nitrodimeethyl-*p*-toluidine, even when the temperature of the concentrated acid solution is raised to 70°. But on pouring this acid liquid into water so that the temperature reaches 40°, further nitration occurs, with the production of a dinitrodimeethyl-*p*-toluidine (m. p. 103—104°) in practically quantitative yield. This dinitro-compound is apparently identical with a by-product of the action of nitrous acid on dimethyl-*p*-toluidine (Pinnow, *Ber.*, *loc. cit.*, p. 2039).

In the present communication the constitution of this dinitro compound has been determined in the following manner.

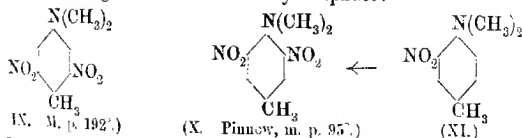
Since the compound can be prepared either directly from *p*-methyl-*p*-toluidine or by the further nitration of 2-nitrodimeethyl-*p*-toluidine (I), it follows that one of the nitro-groups is in position 2 with respect to the methyl radicle:



2-Nitrodimethyl-*p*-toluidine (I), on reduction, yields *as*-4-dimethyl-2:4-tolylendianiline (II), which, when successively acetylated and nitrated, furnishes 5-nitro-2-acetylamino-2:4-tolylendianiline (III). The position of the entrant nitro-group in compound III is ascertained by reduction, when 2-acetyl-2:5-diaminodimethyl-*p*-toluidine (VI) is obtained, and this triamine is converted by the Sandmeyer reaction into 5-bromo-2-acetylamino-2:4-tolylendianiline (V), the constitution of which has been fully established (Morgan and Clayton, *Trans.*, 1905, **87**, 946). But 5-nitro-2-acetylamino-2:4-tolylendianiline (III), when successively reduced and acetylated, gives 2:5-diacetyldiaminodimethyl-*p*-toluidine (IV), and this diacetyl compound can also be produced by reducing dinitrodimethyl-*p*-toluidine (m. p. 103—104°) and acetylating the resulting 2:5-diaminodimethyl-*p*-toluidine (VIII).

These two methods of preparing the same diacetyl compound (IV) prove conclusively that the dinitro-compound melting at 103—104° is 2:5-dinitrodimethyl-*p*-toluidine (VII).

Before the foregoing direct proof was worked out, an indirect method had been adopted, which consisted in preparing 2:6-dinitrodimethyl-*p*-toluidine (IX) and comparing its properties with those of the above-described 2:5-compound. The 2:6-compound is prepared by reducing 2:4:6-trinitrotoluene to 2:6-dinitro-*p*-toluidine, and methylating this base with methyl sulphate:



3:5-Dinitrodimethyl-*p*-toluidine was prepared by Pinnow and Matcovich (*Ber.*, 1898, **31**, 2518) by the action of dilute nitric and sulphuric acids on dimethyl-*p*-toluidine, a chemical change which probably takes place in two stages, for 3-nitrodimethyl-*p*-toluidine

(XI) is formed by the action of aqueous nitrous acid on dimethyl-*p*-toluidine (Pinnow, *Ber.*, 1895, **28**, 3039). It therefore follows that the dinitro-compound melting at 103—104° must be either the 2: 5- or 2: 3-dinitrodimehyl-*p*-toluidine. Reduction to the triamine (VIII) showed that the compound was the 2: 5-isomeride, since the base had all the properties of a para-diamino-compound, and did not react at all like an ortho-diamine.

These results indicate that the nitration of dimethyl-*p*-toluidine takes place in two different ways, depending on the concentration of the acid medium. In strong sulphuric acid, a meta-position to the aminic nitrogen is assumed by the entrant nitro-group, and this formation of 2-nitrodimehyl-*p*-toluidine represents the only stage of nitration so long as the acid remains concentrated. Dilution of the acid with water leads to the introduction of nitro-groups in the ortho-positions with respect to the basic nitrogen atom (compare formulæ VII, X, and XI). In strong acid, the meta-law of substitution is obeyed, whereas nitration in presence of water conforms to the ortho-para law.

These nitration phenomena may be profitably discussed in connexion with the rule put forward by Crum Brown and Gibson (*Trans.*, 1892, **61**, 367) for determining whether a benzenoid mono-derivative shall give a meta-di-derivative or a mixture of ortho- and para-di-derivatives. The rule is applied by considering the hydride of the radicle already present in the molecule, and if this hydride is directly oxidisable to the corresponding hydroxy-derivative, then substitution takes place according to the meta law. For example, the nitro-group, which determines the entry of the second radicle mainly into a meta-position, has the hydride nitrous acid, $\text{H}\cdot\text{NO}_2$, and this is directly oxidisable to nitric acid, $\text{HO}\cdot\text{NO}_2$.

On the other hand, methyl has the hydride methane, $\text{H}\cdot\text{CH}_3$, which is not readily oxidisable to methyl alcohol, $\text{HO}\cdot\text{CH}_3$. In this case the group methyl determines the entry of other radicles into ortho- and para-positions.

This generalisation, although quite empirical, is a remarkably comprehensive rule, and it may be applied successfully to several cases which had not been examined eighteen years ago, when Crum Brown and Gibson first proposed it.

The triazo group N_3 has the hydride $\text{H}\cdot\text{N}_3$ not directly oxidisable to a compound $\text{HO}\cdot\text{N}_3$, and, in accordance with the rule, N_3 induces the entry of other radicles into ortho- and para-positions.

The group AsO_3H_2 present in phenylarsinic acid has the hydride $\text{H}\cdot\text{AsO}_3\text{H}_2$, which is directly oxidisable to arsenic acid, $\text{HO}\cdot\text{AsO}_3\text{H}_2$, and in conformity with the rule this group favours substitution in meta-positions.

The primary benzenoid amines were placed by Crum Brown in the category of substances obeying the ortho-para law; this mode of substitution agreeing with the fact that the hydride $\text{H}\cdot\text{NH}_2$ is not directly oxidisable to hydroxylamine, $\text{HO}\cdot\text{NH}_2$. The generalisation can be extended to the acetyl derivatives; the hydride $\text{H}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3$ is not directly oxidisable to $\text{HO}\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3$, which is in accordance with the fact that the nitration of acetyl derivatives generally follows the ortho-para law.

When, however, the bases are nitrated in strong sulphuric acid, one must consider the group $\text{NH}_2\cdot\text{H}_2\text{SO}_4$ having the hydride $\text{H}\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_4$, which is not directly oxidisable to $\text{HO}\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_4$. In accordance with the Crum Brown and Gibson rule, the presence of this sulphate group should lead to the formation of ortho-para-derivatives, but in many cases substitution occurs by preference in the meta-position. Aniline and dimethylaniline each give products in which the meta-nitro-derivative predominates.

The case of the tertiary bases is of especial interest, because it may be argued that, under certain conditions, the hydride $\text{H}\cdot\text{NR}_2$ is directly oxidisable to $\text{HO}\cdot\text{NR}_2$; thus diethylamine with hydrogen peroxide yields diethylhydroxylamine (Dunstan and Goulding, *Trans.*, 1899, **75**, 1009), and dimethylaniline itself can be oxidised to dimethylaniline oxide. Yet, strangely enough, in dilute solutions, where these tertiary amines may be supposed to be reacting partly in the free state, they nitrate in accordance with the ortho-para law, and only in combination with concentrated sulphuric acid do they react in conformity with the meta law.

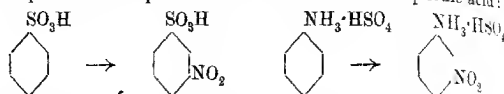
In whichever way the tertiary amines are nitrated, whether in strong or dilute acid, there is a discrepancy between the facts and the application of the Crum Brown and Gibson rule to these phenomena. While indicating this limitation to a rule which has proved fairly general, the authors do not wish to put forward a theory sufficiently comprehensive to include all cases of the nitration of aromatic amines, but they suggest as a working hypothesis that the nitration of an aromatic base or its acetyl derivative is a process essentially different from the nitration of the sulphate of the base in concentrated sulphuric acid (compare Armstrong, *Trans.*, 1887, **51**, 589).

In the former case, the nitric acid is attracted first to the amino- or the acetyl-amino group, giving rise to a nitrate by direct addition; dehydration leads to the production of a nitroamine, and then follows substitution in the sympathetic ortho- and para-positions.

In the latter method of nitration the radicle $\cdot\text{NH}_2\cdot\text{HSO}_4$, $\cdot\text{NHR}_2\cdot\text{HSO}_4$, or $\cdot\text{NHR}_2\cdot\text{HSO}_4$ acts as a strongly acidic group, which, so far from attracting the nitric acid, actually exerts a slight

but appreciable repulsive action, so that the introduction of the nitro-group takes place in the apathetic meta-position, this being shielded from the direct influence of the aminosulphate complex.

The process is comparable to the nitration of a sulphonic acid:



and in both instances the meta-derivatives predominate (compare Flürscheim, *J. pr. Chem.*, 1902, [ii], 66, 324).

This view of the nitration of aromatic amines in concentrated sulphuric acid affords an explanation of the course of substitution in the naphthalene as well as in the benzene series.

EXPERIMENTAL.

Nitration of Dimethyl-p-toluidine.

Dimethyl-*p*-toluidine, dissolved in twelve parts of cold concentrated sulphuric acid and treated with two to three molecular proportions of nitric acid also dissolved in strong sulphuric acid, underwent nitration only to the extent of forming 2-nitrodimethyl-*p*-toluidine (m. p. 37°), for this base separated in practically quantitative yield when the acid solution was poured into ice-cold water or dilute aqueous ammonia.

The nitration proceeded no further than the formation of the mononitro-compound, even when excess of fuming sulphuric and nitric acids were employed at 70°. At higher temperatures, sulphonation and even destructive oxidation set in, but no higher nitro-compounds could be detected.

When, however, the solution of 2-nitrodimethyl-*p*-toluidine in concentrated sulphuric acid, and one molecular proportion of nitric acid was poured into four volumes of water, so that the temperature rose to 40°, further nitration occurred, with the production of 2:5-dinitrodimethyl-*p*-toluidine (m. p. 103–104°), the yield being practically quantitative:

0.1650 gave 0.2872 CO₂ and 0.0742 H₂O. C=47.45; H=5.00.

C₉H₁₁O₄N₂ requires C=47.99; H=4.89 per cent.

2:5-Dinitrodimethyl-*p*-toluidine (VII) can also be prepared by dissolving 2-nitrodimethyl-*p*-toluidine in concentrated nitric and sulphuric acids, and pouring the solution into four volumes of water.

5-Nitro-2-acetylaminodimethyl-p-toluidine (III).

2-Nitrodimethyl-*p*-toluidine was reduced with tin and hydrochloric acid (*Trans.*, 1905, 87, 948), and the resulting 2-aminodimethyl-*p*-toluidine acetylated.

2-Acetylamino-2-methyl-*p*-toluidine was dissolved in 10 parts of concentrated sulphuric acid, and treated with about half its weight of nitric acid (sp. gr. 1.4), diluted with three volumes of strong sulphuric acid. No reaction occurred in the strong acid, but on pouring the solution into water, so that the temperature rose to 70°, nitration set in, and on adding dilute ammonia, 5-nitro-2-acetylamino-2-methyl-*p*-toluidine separated, and was crystallised from alcohol, yielding yellow needles, melting at 155°:

0.1272 gave 0.2594 CO₂ and 0.0768 H₂O. C=55.61; H=6.71.

0.1229 „ 19.0 c.c. N₂ at 18° and 760 mm. N=17.85.

C₁₁H₁₃O₃N₃ requires C=55.63; H=6.32; N=17.72 per cent.

2-Acetyl-2:5-diaminodimethyl-*p*-toluidine (VI).

The foregoing nitroacetyl compound underwent simultaneous reduction and hydrolysis on treatment with tin and hydrochloric acid, and was accordingly reduced with iron filings and water slightly acidified with acetic acid, the reducing agent being slowly added to the boiling solution until the colour disappeared. The solution, after neutralisation with sodium carbonate and filtration, was evaporated to dryness, and the residue, when dissolved in water, crystallised therefrom in colourless crystals, melting at 131–133°:

0.1056 gave 18.2 c.c. N₂ at 16° and 759 mm. N=20.06.

C₁₁H₁₇ON₃ requires N=20.28 per cent.

2-Acetyl-2:5-diaminodimethyl-*p*-toluidine was dissolved in hydrobromic acid containing cuprous chloride, the solution warmed to 80°, and slowly treated with aqueous sodium nitrite (1 mol.). The cooled liquid was rendered ammoniacal, and the precipitate crystallised from alcohol, when it separated in colourless, woolly needles, melting at 163°, and was identified by the method of mixed melting points as 5-bromo-2-acetylamino-2-methyl-*p*-toluidine (V), the constitution of which has already been determined (Trans., 1905, 87, 948).

2:5-Diaminodimethyl-*p*-toluidine (VIII) (compare Pinnow and Mateovich, *loc. cit.*).—Granulated tin was added to a hot solution of 24 grams of 2:5-dinitrodimethyl-*p*-toluidine in 150 c.c. of concentrated hydrochloric acid and 50 c.c. of water until the colour disappeared. After removing the tin as sulphide, the filtrate was evaporated until 2:5-diaminodimethyl-*p*-toluidine hydrochloride separated in colourless crystals. The base set free by ammonia was extracted with chloroform, and on evaporating off the solvent from the carefully dried extract, the triamine was left as an oil, which rapidly oxidised on exposure to the atmosphere and solidified on cooling.

2:5-Diacetyldiaminodimethyl-*p*-toluidine (IV), obtained by treating the preceding base with acetic anhydride, crystallised from very

dilute alcohol in colourless needles, and after repeated crystallisation softened at 233° , and melted at 236° . (Found, $N=16.99$. Calc., $N=16.86$ per cent.)

When heated at 245° for thirty minutes, this diacetyl compound remained unchanged, showing that it was not an ortho-diacetylated compound.

When used in the form of its hydrochloride, 2:5-diaminodimethyl-*p*-toluidine gave the colour reactions of a para-diamine. Oxidation with chromic acid, either alone or in presence of aniline, gave a deep red coloration, indicating the production of a safranine dye. Alkaline hypochlorite, in presence of α -naphthol, led to the production of a blue indophenol. When heated in alcoholic acetic acid solution with phenanthraquinone and sodium acetate, no azine condensation occurred. The triamino underwent diazotisation in acid solution, and the product coupled with alkaline β -naphthol, yielding an azo-derivative. These reactions afforded additional evidence that the triamino has the constitution (VIII) assigned to it on p. 2647. A final confirmation was obtained by preparing 2:5-diacetyldiaminodimethyl-*p*-toluidine by an alternative method, using 2-acetyl-2:5-diaminodimethyl-*p*-toluidine (VI), since the latter compound has been shown to contain its free amino-group in position 5.

2:6-Dinitrodimethyl-*p*-toluidine (IX).

2:6-Dinitro-*p*-toluidine, prepared by reducing 2:4:6-trinitro-toluene with alcoholic ammonium sulphide (Holleman and Böseken, *Rec. trav. chim.*, 1897, **16**, 425), was slowly added to methyl sulphate at 160 – 165° , and the solution maintained at this temperature for thirty minutes. The liquid was then rendered alkaline with sodium hydroxide, and the solid product crystallised from 50 per cent. acetic acid:

0.1307 gave 0.2290 CO_2 and 0.0614 H_2O . $C=47.79$; $H=5.21$.

0.1344 „ 22.2 c.c. N_2 at 23° and 756 mm. $N=18.52$.

$\text{C}_9\text{H}_{11}\text{O}_4\text{N}_3$ requires $C=47.99$; $H=4.89$; $N=18.66$ per cent.

2:6-Dinitrodimethyl-*p*-toluidine separates in yellow needles, melting at 192° .

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The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C₁ group, group, etc.).

Secondly, according to the number of other elements besides carbon contained in a molecule (thus 5 IV indicates that the molecule contains five carbon atoms and five other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Simple metallic salts of acids are indexed under the respective acids.

Simple salts of bases (for example, hydrochlorides, platinumchlorides, and picrates), and described for the purpose of further identifying the base, are indexed under the latter.

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- $C_3H_4O_2N_8$ Bistriazomalonamide (FORSTER and MÜLLER), T., 1085; P., 4.
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5 II

- H_2O Furfuraldehyde, absorption spectrum of (PURVIS), T., 1648; P., 201.
 H_2O Citraconic and itaconic anhydrides, rate of hydration of (RIVETT and SUDGICK), T., 1677; P., 200.
 HN Pyridine, absorption spectra of the vapours of, and its derivatives (PURVIS), T., 692.
 H_2O Methylsuccinic anhydride, rate of hydration of (RIVETT and SUDGICK), T., 1677; P., 200.
 H_2O β -Methoxysuccinic anhydride (PURDIE and YOUNG), T., 1531.
 H_2O β -Methoxysuccinic acid, silver salt of (PURDIE and NEAVE), T., 1518.
 HN 1:4-Dimethylglyoxaline, and its salts (PYMAN), T., 1821; P., 212.
 HN 1:5-Dimethylglyoxaline, and its salts (PYMAN), T., 1823; P., 212.
 HN_2 β -Amino-4-ethylglyoxaline, identity of, with base from ergot (BARGER and DALE), T., 2592; P., 327.
 HN Piperidine, absorption spectrum of the vapour of (PURVIS), T., 705.

5 III

- CH_3ON α -Acetoxyacrylonitrile (DEAKIN and WILSMORE), T., 1969; P., 276.
 CH_3OCl β -Methoxysuccinyl chloride (PURDIE and YOUNG), T., 1530.
 CH_2NBr_2 2:5-Dibromo-1:4-dimethylglyoxaline (PYMAN), T., 1831.
 CH_3OBr Allyl bromoacetate (CLARKE), T., 428.
 CH_3ON Ethyltriazomalononic acid (FORSTER and MÜLLER), T., 133; P., 4.
 CH_2NBr_2 2 (or 5)-Bromo-1:4-dimethylglyoxaline, and its salts (PYMAN), T., 1823; P., 212.
 CH_2NBr_2 4-Bromo-1:5-dimethylglyoxaline, and its salts (PYMAN), T., 1829; P., 212.
 H_2OBr_2 Methyl $\alpha\beta$ -dibromobutyrate (JAMES), T., 1572.
 H_2ON Tetrahydrouic acid, synthesis of (FRANKLAND), T., 1316; P., 171.
 H_2ON Butyryl- and isobutyryl-formamide, synthesis of (BARGER and FRY), T., 291; P., 2.
 H_2ON Ethyltriazomalonamide (FORSTER and MÜLLER), T., 134; P., 4.
 H_2ON β -Methoxysuccinamic acid (PURDIE and YOUNG), T., 1532.
 H_2OBr α -Bromoacetic acid (ALPERS and WEIZMANN), P., 345.

$C_6H_{10}O_2N_2$ *N*-Methoxysuccindiamide (PURDIE and NEAVE), T., 1519.

$C_6H_{10}O_2N_4$ Substance, from triazomethylcarbimide and water (FORSTER and MÜLLER), T., 1063.

C_6 Group.

C_6H_6 Benzene, separation of cyclohexane from mixtures containing (PATTERSON and FLECK), T., 1773; P., 207.

C_6H_{12} cycloHexane, its separation from, and estimation in, mixtures containing benzene (PATTERSON and FLECK), T., 1773; P., 207.

6 II

C_6H_5O Phenol, freezing-point curve for mixtures of camphor and (WOOD and SCOTT), T., 1573; P., 194.

$C_6H_6O_2$ Resorcinol, condensation of benzaldehyde with (POPE and HOWARD), T., 78; condensation of anisaldehyde with (POPE and HOWARD), T., 972; P., 88.

$C_6H_8O_4$ Anhydride of *cis*-tetrahydrofuran-2:5-dicarboxylic acid (LESLIE and HAAS), T., 183.

C_6H_5S Phenyl mercaptan, interaction of, with thionyl chloride (TASKE and JONES), P., 234.

C_6H_5N Aniline, absorption spectra of (PURVIS), T., 1546; P., 194; colorimetric measurement of hydrolysis of salts of (TIZARD), T., 2490; P., 225.

α -Picoline, absorption spectrum of the vapour of (PURVIS), T., 700.

$C_6H_8O_4$ Methyl maleate, action of Grignard reagents on (PURDIE and ARTHUR), T., 1537; P., 199.

$C_6H_8O_4$ *cis*-Tetrahydrofuran-2:5-dicarboxylic acid, ammonium salt of L. (SEEVER and HAAS), T., 183.

δ -Dimethoxysuccinic anhydride (PURDIE and YOUNG), T., 1533.

$C_6H_8O_7$ Citric acid, potassium cupric salts of (PICKERING), T., 1837; P., 11.

$C_6H_9O_5$ Methyl hydrogen *N*-methoxysuccinate (PURDIE and YOUNG), T., 1531.

$C_6H_{12}O$ Methyl *tert*-butyl ketone, action of, on ketols (BOON), T., 1256; P., 4.

$C_6H_{12}O_6$ *D*-Fructose, acetone derivatives of (IRVINE and GARRETT), T., 147; P., 143.

6 III

$C_6H_3O_3N_3$ *s*-Trinitrobenzene, additive compounds of, with arylamines (STUBBROUGH and BEARD), T., 773; P., 71.

$C_6H_3O_3N_5$ Tetranitroaniline (FLÜRSCHHEIM and SIMON), P., 81.

$C_6H_3O_3N_{12}$ Tris-triazomethylisocyanurate (FORSTER and MÜLLER), T., 1064; P., 112.

$C_6H_3O_3N_6$ Ethyl α -bistriazoacetoacetate (FORSTER and NEWMAN), T., 186; P., 197.

$C_6H_3O_3Cl_2$ δ -Dimethoxysuccinyl chloride (PURDIE and YOUNG), T., 1532.

$C_6H_3O_3N_2$ Methyl α -triazomethylacetoacetate (FORSTER and NEWMAN), T., 1863; P., 197.

$C_6H_3O_3Cl$ Methyl α -chloromethylacetoacetate (FORSTER and NEWMAN), T., 1863.

$C_6H_{11}O_2Br$ *n*-Butyl bromoacetate (CLARKE), T., 423.

tert-Butyl bromoacetate (CLARKE), T., 423.

$C_6H_{12}O_4N_6$ Semicarbazone-semicarbazide of acetoacetic acid (CHEN and WILSMORE), T., 1991; P., 217.

6 IV

$C_6H_3O_3I_3S$ 2:3:5-, 2:4:5-, and 3:4:5-Tri-iodobenzenesulphonic acid, metallic salts of (BOYLE), T., 217; P., 4.

$C_6H_3O_3I_2S$ 2:4- and 3:5-Di-iodobenzenesulphonic acid, metallic salts of (BOYLE), T., 216; P., 4.

C₇ Group.

C₇H₈ Toluene, chlorination of (COHEN, DAWSON, BLOCKEY and WOODMANSEY), T., 1623; P., 205.

7 II

- C₇H₄N₄** *m*-Triazobenzonitrile (FORSTER and JUDD), T., 282.
C₇H₆O Benzaldehyde, condensation of resorcinol with (POPE and HOWARD), T., 78.
C₇H₈S Benzyl mercaptan, reactions of (SMYTHE and FORSTER), T., 1195; P., 135.
C₇H₉N Benzylamine, absorption spectrum of (PURVIS), T., 1552.
 Methyl aniline, absorption spectrum of (PURVIS), T., 1551.
 .. and *m*-Toluidine, absorption spectra of (PURVIS), T., 1551.
p-Toluidine, and its condensation product with acetaldehyde, absorption spectra of (PURVIS), T., 684; P., 56.
 2:4 and 2:6-Lutidine, absorption spectra of the vapours of (PURVIS), T., 702.
 Δ^1 -*cyclo*Penteneacetonitrile (HARDING and HAWORTH), T., 491.
C₇H₈O₃ Δ^1 -*cyclo*Penteneacetic acid, and its silver salt (HARDING and HAWORTH), T., 491; P., 61.
*cyclo*Pentylideneacetic acid, and its silver salt (HARDING and HAWORTH), T., 493.
C₇H₈O₃ *cyclo*Hexanone-2-carboxylic acid (GARDNER, PERKIN and WATSON), T., 1764; P., 137.
C₇H₈O₃ *cyclo*Pentan-1-olacetic acid (+ $\frac{1}{2}$ H₂O), and its silver salt (HARDING and HAWORTH), T., 492.
C₇H₈O₄ Ethyl malonate, action of aromatic amines on (CHATTAWAY and ULMSTED), T., 938; P., 69.
C₇H₈O₄ Methyl γ -methoxysuccinate (PURDIE and NEAVE), T., 1517; P., 198; action of Grignard reagents on (PURDIE and ARUP), T., 1537; P., 199.
C₇H₈O₄ Methyl hydrogen α -dimethoxysuccinate (PURDIE and YOUNG), T., 1539.

7 III

- C₇H₄O₄N₄** 2:5 and 2:6-Dinitro-1-methoxy-3:4-quinonediazide (MELDOLA and REVERDIN), T., 1206.
C₇H₅O₃N 5-Nitrosalicylaldehyde, and its sodium salt (CLAYTON), T., 1406.
C₇H₅O₃N *p*-Triazobenz-*anti*- and *syn*-aldoxime (FORSTER and JUDD), T., 257; P., 28.
C₇H₅O₃N₃ 2:3:5-Trinitro-*p*-anisidine (MELDOLA and KUNTZEN), T., 456; P., 58; MELDOLA and REVERDIN, T., 1204; P., 132.
 2:3:5-Trinitro-*p*-anisidine, product of diazotisation of (MELDOLA and REVERDIN), T., 1204; P., 132.
C₇H₅O₃N Phenylcarbamide, action of chlorine on (CHATTAWAY and CHANEY), T., 292; P., 22.
C₇H₅O₃N Ethyl 1-cyanocyclopropane-1-carboxylate (MITCHELL and THORPE), T., 1002.
C₇H₅O₃Br Allyl α -3-dibromobutyrate (JAMES), T., 1572.
C₇H₅O₂Cl₂ α -3-Dichloroacetoacetin (ALFERN and WEIZMANN), P., 345.
C₇H₅O₄N Ethyl bistriazomalonate (FORSTER and MÜLLER), T., 136; P., 4.
C₇H₅O₄Br 1-Bromocyclopentaneacetic acid (HARDING and HAWORTH), T., 492.
C₇H₅O₄N 4-Oximino-*cyclo*hexanecarboxylic acid, optically active, silver and sodium salts of (MILLS and BAIN), T., 1886; P., 214.
 Ethylcarbonate-*isobutyronitrile* (DAVIS), T., 951; P., 90.

- $C_7H_{11}O_3N_3$ Ethyl-*s*-triazomethylacetoacetate, (FORSTER and NEWMAN, T., 1864; P., 197.
 $C_7H_{11}O_2N$ Ethyl N-allylglycine (ALPERN and WEIZMANN), P., 345.
 $C_7H_{11}O_3N_3$ Semicarbazone of homolævulic acid (CAMPBELL and THOMEL, T., 1315.
 $C_7H_{11}NS$ Thioacetylpipeidine (RUSSELL), T., 954.
 $C_7H_{11}ON_2$ Acetenylpipeidyloxime (RUSSELL), T., 955.

7 IV

- $C_7H_5ON_2Cl_6$ 2:4:6-Trichlorophenyltrichlorocarbamide (CHATTAWAY and CHANEY), T., 299.
 $C_7H_5ON_2Cl_5$ 2:4:6-Trichlorophenyldichlorocarbamide (CHATTAWAY and CHANEY), T., 298.
 $C_7H_5ON_2Cl_4$ *p*-Chlorophenyltrichlorocarbamide (CHATTAWAY and CHANEY, T., 295.
 2:4-Dichlorophenyl-*s*-dichlorocarbamide (CHATTAWAY and CHANEY), T., 297.
 2:4-Dichlorophenyl-*as*-dichlorocarbamide (CHATTAWAY and CHANEY, T., 296.
 2:4:6-Trichlorophenylmonochlorocarbamide (CHATTAWAY and CHANEY), T., 297.
 $C_7H_5ON_2Cl_3$ *p*-Chlorophenyldichlorocarbamide (CHATTAWAY and CHANEY, T., 295.
 2:4-Dichlorophenylmonochlorocarbamide (CHATTAWAY and CHANEY, T., 295.
 2:4:6-Trichlorophenylcarbamide (CHATTAWAY and CHANEY), T., 298.
 $C_7H_5O_3I_3S$ Methyl 2:3:5-, 2:4:5-, and 3:4:5-tri-iodobenzenesulphonate (BOYLE), T., 218; P., 4.
 $C_7H_5ON_2Cl_2$ *p*-Chlorophenylchlorocarbamide (CHATTAWAY and CHANEY, T., 294.
 $C_7H_5O_3I_2S$ Methyl 2:4-, 2:5-, 3:4-, and 3:5-di-iodobenzenesulphonate (BOYLE), T., 216, 220; P., 4.
 $C_7H_5O_2N_2S$ Methanesulphonyl-*p*-phenylenediazomide (MORGAN, PICKARD and MICKLETHWAIT), T., 62.
 $C_7H_5O_2N_2S$ Methanesulphonyl-*p*-nitroaniline (MORGAN, PICKARD, and MICKLETHWAIT), T., 61.
 $C_7H_5O_2N_2S$ Methanesulphonyl-*p*-phenylenediamine and its hydrochloride (MORGAN, PICKARD, and MICKLETHWAIT), T., 61.

C₈ Group.

- $C_8H_6O_3$ Phthalic anhydride, rate of hydration of (RIVETT and SIDGWICK), T., 1877; P., 200.
 $C_8H_8O_2$ Anisaldehyde, condensation of, with resorcinol (POPE and HOWARD, T., 972; P., 88.
 $C_8H_8O_2$ 4-Methoxy-2:5-toluquinone (LUFF, PERKIN, and ROBINSON), T., 1127; P., 132.
 $C_8H_8O_2$ 4-Methoxy-2:5-toluquinol (LUFF, PERKIN, and ROBINSON), T., 1128.
 C_8H_9N Ethylaniline, absorption spectrum of (PURVIS), T., 1551.
 Dimethylaniline, absorption spectrum of (PURVIS), T., 1551.
 o-3-, and *m*-2-Xylidine, absorption spectra of (PURVIS), T., 1552.
 2:4:6-Trimethylpyridine, absorption spectrum of the vapour of (PURVIS, T., 704.
 $C_8H_{13}O_2$ *d*-1-Methyl- Δ^3 -cyclohexene-3-carboxylic acid (PERKIN), P., 97.
 dl-, *d*-, and *l*-1-Methyl- Δ^3 -cyclohexene-3-carboxylic acids, and calcium salt of the first (PERKIN), T., 2138, 2140, 2142.

- $C_8H_8O_4$ 1-Methylcyclohexan-2-one-3-carboxylic acid (GARDNER, PERKIN, and WATSON), T., 1765; P., 137.
 β , and δ -1-Methylcyclohexan-3-one-4-carboxylic acids (GARDNER, PERKIN, and WATSON), T., 1767; P., 137.
 β -Methylcyclohexan-4-one-3-carboxylic acid (GARDNER, PERKIN, and WATSON), T., 1769; P., 137.
 $C_5H_8O_6$ Pentane- $\alpha\beta\delta$ -tricarboxylic acid (HOPE and PERKIN), P., 178.
 β -Pentane- $\alpha\beta\delta$ -tricarboxylic acid (HOPE and PERKIN), P., 178.
 $C_8H_8O_4$ 1-Methylcyclohexan-2-ol-3-carboxylic acid (GARDNER, PERKIN, and WATSON), T., 1766.
 α , and δ -1-Methylcyclohexan-3-ol-4-carboxylic acids (GARDNER, PERKIN, and WATSON), T., 1767.
 β -Methylcyclohexan-4-ol-3-carboxylic acid (GARDNER, PERKIN, and WATSON), T., 1770; P., 137.
 $C_8H_9O_2$ Acid, from oxidation of carpaine (BARGER), T., 471.
 C_8H_7N Conine, absorption spectra of (PURVIS), T., 1035; P., 113.

8 III

- $C_8H_4O_4Cl_2$ 3,5-Dichloro-*o*-phthalic acid, synthesis of (CROSSLEY and WREN), T., 58; P., 8.
 $C_8H_8O_4N_2$ 2,5-Dinitro-4-acetyl-amino-3-triazophenol (MELDOLA and KUNTZEN), P., 340.
 $C_8H_8O_4N_4$ 2,3,5-Trinitro-4-acetyl-amino-phenol, metallic salts of, and absorption spectrum of (MELDOLA and KUNTZEN), T., 444; P., 58.
 $C_8H_8ON_2$ Triazoacetophenone, and its derivatives (FORSTER and MÜLLER), T., 140.
 $C_8H_8ON_2$ Phenyltriazooacetic acid (FORSTER and MÜLLER), T., 138; P., 4.
 C_8H_8OCl α -Chloro-*o*-hydroxyacetophenone (TUTIN), T., 2504.
 C_8H_8ON 3-Nitro-7-methylsalicylaldehyde (CLAYTON), T., 1405.
 C_8H_8ON 4-Nitro-4-methylsalicylaldehyde (CLAYTON), T., 1406.
 $C_8H_8ON_2$ α -Triazogallacetophenone (BARGER and EWINS), T., 2260.
 C_8H_8ON 5-Nitro-4-methylsalicylic acid (CLAYTON), T., 1402.
 $C_8H_8ON_2$ Phenyliminoacetamidic (FORSTER and MÜLLER), T., 140.
 $C_8H_8ON_2$ Triazoacetophenoneoxime (FORSTER and MÜLLER), T., 141.
 $C_8H_8ON_2$ Oxime of 5-nitro-4-methylsalicylaldehyde (CLAYTON), T., 1406.
 C_8H_8ON Phenyltriazomethylcarbamide (FORSTER and MÜLLER), T., 1065; P., 113.
 C_8H_8ON α -Amino-*p*-hydroxyacetophenone, hydriodide of (TUTIN), T., 2520.
 α -Cyano- Δ^1 -cyclopenteneacetic acid (HARDING and HAWORTH), T., 489; P., 61.
 C_8H_8ON α -Amino-*op*-dihydroxyacetophenone, and its salts, (TUTIN), T., 2513; P., 245.
 α -Amino-*mp*-dihydroxyacetophenone, hydriodide of (TUTIN), T., 2520; P., 244.
 C_8H_8ON 5-Nitro-2-ethoxybenzaldehyde (CLAYTON), T., 2109.
 α -Aminogallacetophenone, hydrochloride of (BARGER and EWINS), T., 2261; P., 248.
 $C_8H_8ON_2$ Substance, from phenyltriazomethylcarbamide and sodium carbonate (FORSTER and MÜLLER), T., 1065.
 C_8H_8ON 2,3,4-Trihydroxy-*S*-phenylethylamine, hydrochloride of (BARGER and EWINS), T., 2260; P., 248.
 C_8H_8OCl 5-Chloro-1:1-dimethyl- Δ^1 -cyclohexen-3-one, interaction of ethyl cyanoacetate and (CROSSLEY and GILLING), T., 518; P., 53.

- $C_6H_{11}O_2N$ Ethyl 1-cyanocyclobutane-1-carboxylate, preparation of pure (CAMPELL and THORPE), T., 2421.
 3:4-Dihydroxy- β -phenylethylamine, preparation of, and its hydrobromide. (BARGER and EWINS), T., 2257; P., 248.
 $C_6H_{12}O_2N_2$ Ethyl β -imino- α -cyanovaleate (CAMPELL and THORPE), T., 1308.
 $C_6H_{12}O_2Br_2$ 3:4-Dibromo-1-methylcyclohexane-3-carboxylic acid (LUFF and PERKIN), T., 2152.
 $C_6H_{12}O_2N_2$ 4-Amino-2:4-dimethyl- Δ^2 -tetrahydro-6-pyridone-3-carboxylamide, and its silver and barium salts (CHICK and WILSMORE), T., 1663; P., 217.
 $C_6H_{12}O_2Br$ 4-Bromo-1-methylcyclohexane-3-carboxylic acid (LUFF and PERKIN), T., 2153.
 $C_6H_{12}O_2N_2$ Ethyl α -triazethylacetacetate (FORSTER and NEWMAN), T., 1365; P., 197.
 $C_6H_{12}O_4N_3$ Ethyl methyltriazomalonate (FORSTER and MÜLLER), T., 132; P., 4.
 $C_6H_{11}O_2N_2$ Semicarbazone of ethyl α -triazomethylacetacetate (FORSTER and NEWMAN), T., 1365.

8 IV

- $C_6H_5ON.K$ Substance, from *p*-triazobenzaldehyde and potassium cyanide (FORSTER and JUDG), T., 260.
 $C_6H_4O_3I_3S$ Ethyl 2:3:5-, 2:4:5-, and 3:4:5-triiodobenzenesulphonate (BOYLE), T., 217; P., 4.
 $C_6H_4O_3I_2S$ Ethyl 2:4-, 2:5-, 3:4-, and 3:5-diiodobenzenesulphonate (BOYLE), T., 216, 220; P., 4.

C₉ Group.

- C_9H_{16} *cyclo*Geraniolene, synthesis of (CROSLLEY and GILLING), T., 741; P., 252.

9 II

- $C_9H_8O_1$ Triketohydrindene hydrate (RHEMANN), T., 1446, 2025; P., 194, 235.
 C_9H_7N Quinoline, absorption spectra of (PURVIS), T., 1035; P., 113; *p*-hydroxyazo-derivatives of (FOX), T., 1337; P., 177.
 C_9H_8O α -Hydrindone, preparation of (MITCHELL and THORPE), T., 2274.
 $C_9H_5O_3$ Coumarinic acid, constitution of (CLAYTON), T., 2102; P., 230.
 $C_9H_8N_2$ 3-Aminoquinoline, and its salts (MILLS and WATSON), T., 746; P., 36.
 $C_9H_7Cl_4$ $\alpha\beta\gamma\gamma$ -Tetrachloro- α -phenylpropane (CLARKE), T., 898; P., 95.
 C_9H_9Br Cinnamyl bromide (CLARKE), T., 428.
 $C_9H_9O_2$ 4:5- and 5:6-Dimethylsalicylaldehyde (CLAYTON), T., 1404.
 $C_9H_9O_3$ α -Hydroxy- α -phenylpropionic acid, optically active, the interconversion of, and its silver salt (MCKENZIE and CLOUGH), T., 1016; P., 84; conversion of, into α -chloro- α -phenylpropionic acid (MCKENZIE and CLOUGH), T., 2564; P., 325.
 α -Hydroxy- β -phenylpropionic acids, optically active, interconversion of (MCKENZIE and WREN), T., 1355; P., 181.
d- and *l*- β -Hydroxy- β -phenylpropionic acid (MCKENZIE and HUMPHREY), T., 123.
 5:6-Dimethylsalicylic acid (CLAYTON), T., 1405.
 Methyl *l*-mandelate, optically active glycols from (MCKENZIE and WREN), T., 473; P., 54.

- CH₃N₃, *p*-Amino-*m*-tolylacetoneitrile, and its hydrochloride and oxalate (BARGER and EWINS), T., 2256.
 CH₃N₃, *m*-Xylidine, and its condensation product with acetaldehyde, absorption spectra of (PURVIS), T., 644; P., 56.
 CH₃N₃, Mesidine, absorption spectrum of (PURVIS), T., 1552.
 CH₃O, 1-Methyl-Δ²-cyclohexene-3-acetonitrile (HARDING and HAWORTH), T., 495.
 CH₃O, 1-Methyl-Δ²-cyclohexene-3-acetic acid (HARDING and HAWORTH), T., 495.
 CH₃O, Ethyl Δ²-cyclopenteneacetate (HARDING and HAWORTH), T., 493.
 CH₃O, Acid, from the sodio-derivative of dimethyl α-thujadiacrylate, and its silver salt (THOMSON), T., 1515; P., 178.
 CH₃O, Δ²-Nonenoic acid, and its derivatives (HARDING and WEIZMANN), T., 299; P., 24.
 CH₃O, Ethyl *l*-methoxysuccinate (PURDIE and NEAVE), T., 1518.
 CH₃O, Dipropionin (ALFERN and WEIZMANN), P., 345.
 CH₃O, α- and β-Fructosemonooacetone (IRVINE and GARNETT), T., 1283; P., 143.
 CH₃Br, 3-Bromo-1:1:3-trimethylcyclohexane (CROSSLEY and GILLING), T., 2220.
 CH₃O, 1:1:3-Trimethylcyclohexan-3-ol (CROSSLEY and GILLING), T., 2220; P., 232.
 CH₃O, *n*-Nonoic acid, condensation products of, with glycine, alanine and leucine (HOPWOOD and WEIZMANN), P., 69.
 CH₃O, β-Hydroxy-*n*-nonoic acid (HARDING and WEIZMANN), T., 303.

9 III

- CH₃ON, 3:6- and 6:8-Dinitrocoumarin (CLAYTON), T., 1397.
 CH₃ON, 6:8-Dinitroumbelliferone (CLAYTON), T., 1401.
 CH₃ON, 8-Nitroumbelliferone (CLAYTON), T., 1401.
 CH₃OCl, ααβ-Trichloro-β-phenylpropionyl chloride (CLARKE), T., 893; P., 96.
 CH₃ON, 6:8-Dinitrocoumarinic acid (CLAYTON), T., 1407.
 CH₃ON, 8-Hydroxyquinoline, and its sulphate (MILLS and WATSON), T., 753; P., 56.
 CH₃ON, 8-Hydroxyquinoline, metallic salts of (FOX), T., 1119; P., 134.
 CH₃OCl, αβ-Dichloro-β-phenylpropionyl chloride (CLARKE), T., 892; P., 96.
 CH₃ON, 8-Aminoconmarin (CLAYTON), T., 1352.
 CH₃OCl, ααβ-Trichloro-β-phenylpropionic acid (CLARKE), T., 891; P., 96.
 CH₃ON, Phenyltriazomalononic acid (FORSTER and MÜLLER), T., 134; P., 1.
 CH₃OCl, α-Chloro-3:4-dihydroxyinnamic acid (CLARKE), T., 897; P., 96.
 CH₃ON, 8-Nitrocoumarinic acid, silver salt (CLAYTON), T., 2106.
 CH₃ON, 8-Nitro-7-hydroxyconmarinic acid (CLAYTON), T., 1408.
 CH₃ONCl, 2-Chloro-8-aminoquinoline (MILLS and WATSON), T., 754; P., 56.
 CH₃OCl, αβ-Chloro-α-phenylpropionyl chloride (MCKENZIE and CLOUGH), T., 1021.
 CH₃ON, *p*-Nitro-*m*-tolylacetoneitrile (BARGER and EWINS), T., 2256.
 CH₃ON, 3:6-Dinitro-4:5-dimethylsalicylaldehyde (CLAYTON), T., 1407.
 CH₃ON, 3:6-Dinitro-4:5-dimethylsalicylic acid (+ ½H₂O) (CLAYTON), T., 1402.
 CH₃ON, 2:3:5-Trinitro-4-acetylaminobenzole (MELDOLA and KUNTZEN), T., 435; P., 58.
 CH₃ON, *p*-Hydroxy-*m*-tolylacetoneitrile (BARGER and EWINS), T., 2256.

- $C_9H_9O_2N$ *syn*-Ethylidenesalicylamide (HICKS), T., 1034; P., 92.
 2-Methyl-1:3-dihydrobenzoxazine-1-one (HICKS), T., 1032; P., 91.
 $C_8H_7O_2N_5$ Phenyltriazomalona^hamide (FORSTER and MÜLLER), T., 1338; P., 4.
 $C_6H_5O_2Cl$ *d*- and *l*- α -Chloro- α -phenylpropionic acid (McKENZIE and CLOUGH), T., 1021.
 ω -Chloro-*o*-methoxyacetophenone (TUTIN), T., 2503; P., 244.
 $C_8H_7O_2Br$ Benzyl bromoacetate (CLARKE), T., 428.
 $C_8H_7O_2N$ Malonanilic acid, preparation of (CHATTAWAY and OLIVIER), T., 339.
 $C_8H_7O_2N$ 3-Nitro-4:5- and 5:6-dimethylsalicylaldehyde (CLAYTON), T., 1405.
 $C_8H_{10}ON_6$ Triazoacetophenonesemicarbazone (FORSTER and MÜLLER), T., 141.
 $C_8H_{11}O_2N$ Methyl α -cyano- Δ^1 -cyclopenteneacetate (HARDING and HAWORTH), T., 490.
 ω -Amino-*p*-methoxyacetophenone, salts of (TUTIN), T., 2509.
 $C_8H_{11}O_2N_2$ 2:5-Dinitrodimethyl-*p*-toluidine (MORGAN and CLAYTON), T., 2650; P., 323.
 2:6-Dinitrodimethyl-*p*-toluidine (MORGAN and CLAYTON), T., 2652; P., 323.
 $C_8H_{11}O_2N_2$ 2:6-Dinitrodimethyl-*p*-anisidine (MELDOLA), P., 232.
 $C_8H_{11}O_2N_7$ Guanidine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 452.
 $C_8H_{11}NS$ *N*-Methylthiodiphenylamine, mercuri-iodide of (BARNETT and SMILES), T., 985.
 $C_8H_{11}ON$ *p*-Hydroxyphenylethylmethylamine, and its hydrochloride, picrate, oxalate and piconolate (WALFORD), T., 945; P., 88.
 4-Hydroxy- β -*m*-tolylethylamine, and its salts (BARGER and EWING), T., 2257; P., 248.
 $C_8H_{13}ON$ β -Amino- β -phenoxyisopropyl alcohol, and its salts (BOTH), T., 1791; P., 209.
 3:4-Dihydroxyphenylethylmethylamine, and its salts (PYMAN), T., 272.
 4:5-Dimethoxy-*o*-toluidine (LUFF, PECKIN, and ROBINSON), T., 1134; P., 132.
 $C_8H_{13}O_2N$ Ethyl cyanoisobutylacetate, and its silver salt (CAMPELL and THORPE), T., 1311.
 $C_8H_{13}O_2N_2$ Ethyl β -imino- α -cyanoisobutylacetate (CAMPELL and THORPE), T., 1311.
 $C_8H_{13}OCl$ Δ^2 -Nonenoyl chloride (HARDING and WEIZMANN), T., 302.
 $C_8H_{13}O_2Br$ Ethyl 1-bromocyclopentaneacetate (HARDING and HAWORTH), T., 493.
 $C_8H_{12}O_2N$ Amide of α -thujadicarboxylic acid, and its ammonium salt (THOMSON), T., 1512.
 $C_8H_{12}O_2N_3$ Ethyl ethyltriazomalona^hte (FORSTER and MÜLLER), T., 1338; P., 4.
 $C_8H_{12}O_2Br_2$ α , β -Dibromo-*n*-nonoic acid (HARDING and WEIZMANN), T., 304.
 $C_8H_{10}O_2N_6$ Semicarbazone of ethyl α -triazoeethylacetate (FORSTER and NEWMAN), T., 1366.
 $C_8H_{11}ON$ Δ^2 -Nonenoamide (HARDING and WEIZMANN), T., 302.

9 IV

- $C_8H_6O_3NCl_2$ 2:4:6-Trichloromalonanilic acid (CHATTAWAY and MASON), T., 343.
 $C_8H_6O_3NBr_2$ 2:4:6-Tribromomalonanilic acid (CHATTAWAY and MASON), T., 345.
 $C_8H_6O_3NCl_2$ 2:4-Dichloromalonanilic acid (CHATTAWAY and MASON), T., 343.

- C_6H_4ONBr 2,4-Dibromomalonanilic acid (CHATTAWAY and MASON), T., 344.
 C_6H_4ONCl *p*-Chloromalonilic acid (CHATTAWAY and MASON), T., 341.
 C_6H_4ONBr *p*-Bromomalonanilic acid (CHATTAWAY and MASON), T., 344.
 C_6H_5OCiBr α -Bromo- α -nonyl chloride (HOPWOOD and WEIZMANN), P., 69.

C₁₀ Group.

- $C_{10}H_8$ Naphthalene, absorption spectrum of (HOMER and PERVIS), T., 280 ; P., 5; the Friedel-Crafts' reaction applied to (HOMER), T., 1141 ; P., 11.
 $C_{10}H_8$ 1,4-Dihydronaphthalene, absorption spectrum of (LEONARD), T., 1246 ; P., 113.
 $C_{10}H_8$ 1,2,3,4-Tetrahydronaphthalene, absorption spectrum of (LEONARD), T., 1216 ; P., 143.
 $C_{10}H_{16}$ Terpene, monocyclic, from thymol (HENDERSON and SUTHERLAND), T., 1619 ; P., 203.
 $\Delta^{1,2,3,4}$ -Menthadiene, new method of preparation of (PERKIN and WALLACH), T., 1127 ; P., 194.
 $\Delta^{1,2,3,4}$ -*m*-Menthadiene (PERKIN), T., 2147.
 $\Delta^{1,2,3,4}$ -*m*-Menthadiene (PERKIN), T., 2139, 2142.
 Δ^1 -Carevitrene (*sylvestrene*), synthesis of, and its dihydrochloride (PERKIN), P., 57.
 $C_{10}H_{18}$ 1,1-Dimethyl-3-ethylcyclohexene (CROSSLEY and GILLING), T., 2222.
 $C_{10}H_{18}$ Dihydrocamphene, preparation of (HENDERSON and POLLOCK), T., 1621 ; P., 203.
 $C_{10}H_{18}$ Dihydrobornylene, preparation of (HENDERSON and POLLOCK), T., 1621 ; P., 203.

10 II

- H_2O Mellophanic acid (*benzene-1:2:3:4-tetracarboxylic acid*), constitution of (BAMFORD and SIMONSEN), T., 1908 ; P., 206.
 H_2O Prehnitic acid (*benzene-1:2:3:5-tetracarboxylic acid*), constitution of (BAMFORD and SIMONSEN), T., 1906 ; P., 206.
 H_2N_2 2,7-Bis-triazonaphthalene (*naphthylene-2:7-bisazoinide*) (MORGAN and MCKEITHWAIT), T., 2560 ; P., 293.
 H_2N_2 1,2-Naphthylenediazoimine, two isomerides (MORGAN and GODDEN), T., 1718.
 H_2O Methyltrimesic acid, and its silver salt (SIMONSEN), T., 1914 ; P., 209.
 H_2N 1-Imino-2-cyanohydrindene (MITCHELL and THORPE), T., 2270.
 H_2O 4,6-Phenyl-8-methylglycidic acid, sodium salt (WOOTTON), T., 409 ; P., 44.
 H_2O 2-Methyl-1-hydrindone (MITCHELL and THORPE), T., 2275.
 H_2O *m*-Hemipinic acid, preparation of (LUFF, PERKIN, and ROBINSON), T., 1136 ; P., 132.
 H_2O 3,5-Diethyl-*p*-benzoquinone (HENDERSON and BOYD), T., 1664.
 H_2O Methyl *p*-phenylmethoxyacetate (McKENZIE and WREN), T., 484.
 H_2O 8,5-Hydroxy-3-methoxyphenylpropionic acid (SALWAY), T., 2417.
 H_2O 3,4-Trimeethoxybenzaldehyde (BARGER and EWINS), T., 2258.
 H_2O Asaronic acid, preparation of (LUFF, PERKIN, and ROBINSON), T., 1138 ; P., 132.
 H_2N 3,6-Aminoethylindole, syntheses of (EWINS and LAIDLAW), P., 343.
 H_2N 2-Methyltetrahydroquinoline (*tetrahydroquinoline*), racemic, resolution of (POPE and READ), T., 2199 ; P., 251.
 H_2O 1,2-Methyltetrahydroquinoline, and their hydrochlorides (POPE and READ), T., 2203.

- $C_{11}H_{14}O$ Methylpropylphenol (HENDERSON and BOYD), T., 1669.
 $C_{10}H_{14}O_3$ *l*- α , β -Dihydroxy- α -phenylisobutane (McKENZIE and WREN), T., 451.
 3,5-Diethylquinol (HENDERSON and BOYD), T., 1665.
 $C_{15}H_{15}O_3$ 2,4:5-Trimethoxytoluene (LUFF, PERKIN, and ROBINSON), T., 1157; P., 133.
 $C_{10}H_{14}O_4$ Tetrahydroxytert.-butylbenzene (HENDERSON and BOYD), T., 1665.
 Tetrahydroxycymene (HENDERSON and BOYD), T., 1663.
 $C_{10}H_{11}N_2$ Nicotine, absorption spectra of (PURVIS), T., 1935; P., 113.
 $C_{10}H_{15}N$ Diethylaniline, absorption spectrum of (PURVIS), T., 1551.
 α -1-Methyl- Δ^2 -cyclohexene-3-propionitrile (HARDING and HAWORTH), T., 496.
 $C_{10}H_{18}O$ Camphor, vapour pressure of (VANSTONE), T., 429; P., 47; absorption spectra of the acyl-derivatives of (LOWRY and SOUTHGATE), T., 905; P., 65; freezing-point curve for mixtures of, and phenol (WOOD and SCOTT), T., 1573; P., 194; mercury compounds of, action of halogens on (MANSU), T., 2419; P., 297.
 Tanacetone (β -thujone), and its derivatives (THOMSON), T., 1502; P., 177.
 $C_{10}H_{16}O_2$ α -1-Methyl- Δ^2 -cyclohexene-3-propionic acid (HARDING and HAWORTH), T., 497.
 Ethyl *d*-1-methyl- Δ^1 -cyclohexene-3-carboxylate (PERKIN), P., 97.
 Ethyl 1-methyl- Δ^4 -cyclohexene-3-carboxylate (PERKIN), T., 2143.
 Ethyl *dl*-, *d*-, and *l*-1-methyl- Δ^2 -cyclohexene-3-carboxylate (PERKIN), T., 2139, 2140, 2143.
 $C_{10}H_{16}O_3$ Ethyl *dl*- and *d*-methylcyclohexan-3-one-4-carboxylates (GALLAGHER, PERKIN, and WATSON), T., 1767.
 $C_{10}H_{16}O_4$ Camphoric acid, Komppa's synthesis of (BLANC and THORPE), T., 534; P., 83; synthesis of (KOMPPA), P., 328; mono-aryl esters of (EDMONSON and HILDITCH), T., 224; action of the Grignard reagent on esters of (SHIBATA), T., 1239; P., 141.
 β -Camphoric acid, action of the Grignard reagent on esters of (SHIBATA), T., 1239; P., 141.
 Lactone of α -methyl- γ -hydroxyisopropyladipic acid, *cis*- and *trans*- (PERKIN), T., 2144.
 $C_{10}H_{18}O$ Borneol, vapour pressure of (VANSTONE), T., 429; P., 47.
 Δ^2 -*p*-Menthénol(8), new method of preparation of (PERKIN and WALLACE), T., 1427; P., 194.
 dl - Δ^4 -*m*-Menthénol(8) (PERKIN), T., 2147.
 dl -, *d*-, and *l*- Δ^5 -*m*-Menthénol(8) (PERKIN), T., 2139, 2141, 2143.
 d -Dihydrocarvestrenol (PERKIN), P., 97.
 $C_{10}H_{18}O_3$ Ethyl 1-methylcyclohexan-4-ol-3-carboxylate (GARDNER, PERKIN, and WATSON), T., 1770.
 $C_{10}H_{18}Br$ 3-Bromo-1:1-dimethyl-3-ethylcyclohexane (CROSSLEY and GILLING), T., 2222.
 $C_{10}H_{20}O$ 1:1-Dimethyl-3-ethylcyclohexan-3-ol (CROSSLEY and GILLING), T., 2222.
 $C_{10}H_{20}O_2$ Menthan-2:5-diol (HENDERSON and SUTHERLAND), T., 1618; P., 293.
 $C_{10}H_{20}O_4$ γ , δ -Dimethoxy- β -dimethylhexane- β , ϵ -diol (PURDIE and YOUNG), T., 1534; P., 198.

10 III

- $C_{10}H_8O_2N$ Substance, from triketohydrindene and hydrogen cyanide (BUEMANN), T., 2029; P., 235.
 $C_{10}H_8O_4Cl_2$ α , β -Dichloro-3:4-dichloromethylenedioxy- β -phenylpropene chloride (CLARKE), T., 896; P., 96.

- $C_9H_7O_2Cl$ α -Chloro-3:4-carboxyldioxy-cinnamic acid (CLARKE), T., 897; P., 96.
- $C_9H_7O_2Br$ Dibromoscopoletin (MOORE), T., 2229.
- $C_9H_7O_2Cl$ $\alpha\beta$ -Dichloro-3:4-carboxyldioxy- β -phenylpropionic acid (CLARKE), T., 896; P., 96.
- $C_9H_7O_2N$ 3:6-Dinitro-7-methylcoumarin (CLAYTON), T., 1398.
- $C_9H_7N_2Br$ 4-Bromonaphthylene-1-diazo-2-imine (MORGAN and GODDEN), T., 1712.
- C_9H_7ON 2-Cyano-1-hydrindone (MITCHELL and THORPE), T., 2277.
- C_9H_7ON 6-Nitro-7-methylcoumarin (CLAYTON), T., 1397.
- 5-Nitro-7-methylcoumarin (CLAYTON), T., 1406.
- C_9H_7ON Quinoline-3-carboxysamide (MILLS and WATSON), T., 745; P., 56.
- C_9H_7NI 4-Iodo- α -naphthylamine (MORGAN and GODDEN), T., 1717.
- C_9H_7ON Benzoyl-lactonitrile (DAVIS), T., 959; P., 89.
- C_9H_7ON 7-Amino-7-methylcoumarin (CLAYTON), T., 1352.
- $C_9H_7O_2Cl$ Methyl $\alpha\alpha\beta$ -trichloro- β -phenylpropionate (CLARKE), T., 895; P., 96.
- $C_{10}H_8O_2N_2$ Substance, from guanidine and triketohydrindene (RUHEMANN), T., 2028; P., 235.
- $C_{10}H_8O_2N$ Methyl ether of 5-nitrocoumaric acid, silver salt of (CLAYTON), T., 2103.
- Methylether of 5-nitrocoumarinic acid, and silver salt (CLAYTON), T., 2107.
- $C_{10}H_8N_2Br$ 4-Bromo-1:2-naphthylenediamine (MORGAN and GODDEN), T., 1710.
- $C_{10}H_8O_2N_2$ α -5-Dinitro-2-hydroxy- α -4-dimethylstyrene, and its sodium salt (CLAYTON), T., 1407.
- $C_{10}H_8O_2N$ 4:5-Dimethoxy- σ -toluonitrile (LUFF, PERKIN, and ROBINSON), T., 1135; P., 132.
- Phenolbetaine of 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium hydroxide (and + H_2O and $1\frac{1}{2}H_2O$) (PYMAN), T., 276.
- $C_{10}H_8O_2N$ Ethyl phenyltriazooacetate (FORSTER and MÜLLER), T., 138; P., 4.
- $C_{10}H_8O_2N$ Malono- σ - and p -toluidic acid, preparation of (CHATTAWAY and OLSTED), T., 940.
- 6:7-Dihydroxy-1-keto-2-methyltetrahydroisoquinoline (PYMAN), T., 271.
- $C_{10}H_8O_2Cl$ α -Chloro- op -dimethoxyacetophenone (TUTIN), T., 2512; P., 244.
- α -Chloro- mp -dimethoxyacetophenone (TUTIN), T., 2510; P., 244.
- $C_{10}H_8N_2Fe$ Tetramethyl ferrocyanide, derivatives of (HARTLEY), T., 1066, 1725; P., 90, 210.
- $C_{10}H_8O_2N$ α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetic acid (HARDING and HAWORTH), T., 494.
- Ethyl α -cyano- Δ^1 -cyclopenteneacetate (HARDING and HAWORTH), T., 489; P., 61.
- Methyl α -cyano- α - Δ^1 -cyclopentenepropionate (HARDING and HAWORTH), T., 490.
- 3:5-Diethyl- p -benzoquinone oxime (HENDERSON and BOYD), T., 1664.
- 6:7-Dihydroxy-2-methyltetrahydroisoquinoline, and its hydrochloride and picrate (PYMAN), T., 275.
- $C_{10}H_8O_2Cl$ 7-Chloro-8-hydroxy- α - σ - and p -tolylloxypropane (BOYD and MARLE), T., 1790; P., 208.
- $C_{10}H_8O_2N$ 3-Methoxy-4:5-methylenedioxyphenylethylamine, and its hydrochloride (SALWAY), T., 1212.
- Ethyl α -cyano- β -cyclohexylformylacetate (CAMPBELL and THORPE), T., 2424.

- $C_{10}H_{13}ON$ β -5-Hydroxy-3-methoxyphenylpropionamide (SALWAY), T., 2417.
6:7-Dihydroxy-2-methyl-3:4-dihydroisoquinolinium hydroxide, its chloride, picrate, and sodium salt (PYMAN), T., 276.
- $C_{10}H_{13}O_2N_2$ Ethyl β -imino- α -cyano- β -cyclobutylpropionate (CAMPBELL and THORPE), T., 2424.
- $C_{10}H_{13}O_2N_2$ Ethyl β -imino- α -cyanoglutarate, constitution of (CAMPBELL and THORPE), T., 1299; P., 176.
Ethyl hydrogen β -imino- α' -cyano- $\alpha\alpha$ -dimethylglutarate (CAMPBELL and THORPE), T., 1311.
- $C_{10}H_{15}ON$ *p*-Hydroxyphenylethylethylamine, and its oxalate, hydrochloride and picronolate (WALPOLE), T., 948; P., 88.
- $C_{10}H_{15}O_2N$ 3:4-Dihydroxyphenylethylethylamine, and its hydrochloride (PYMAN), T., 274.
Camphorimide, *N*-alkyl and aryl derivatives of (WOOTTON), T., 415.
d-Camphorimide, preparation of, and its derivatives (EVANS), T., 2237; P., 251.
- $C_{10}H_{16}ON_2$ α - and β -Camphorquinonehydrazone (FOSTER and ZIMMEL), T., 2165; P., 245.
- $C_{10}H_{16}O_2S_2$ Camphor- β -thiosulphonic acid, and its sodium salt (HILDITCH), T., 1098; P., 96.
- $C_{10}H_{16}O_2S$ Camphor- β -sulphonic acid, mono-aryl esters of (EDMONSON and HILDITCH), T., 228.
d- and *l*-Camphor- β -sulphonic acid, *d*- and *l*-pavine and metallic salts of, rotatory power of (POPE and GIBSON), T., 2211; P., 250.
d- and *l*-Camphor- π -sulphonic acid, ammonium salts of (POPE and REAR), T., 990.
- $C_{10}H_{17}ON$ Dimethylethylcyclohexanoneoxime (CROSSLEY and GILLING), T., 534.
- $C_{10}H_{17}O_2N$ α -Camphoramic acid, alkyl and aryl derivatives of (WOOTTON), T., 413.
- $C_{10}H_{19}ON$ 3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-propionitrile (CROSSLEY and GILLING), T., 534.

10 IV

- $C_{10}H_6O_2N_2Cr_2$ Naphthalene-2:7-bisdiazonium dichromate (MORGAN and MICKLETHWAIT), T., 2558; P., 293.
- $C_{10}H_6N_2ClPt$ Naphthalene-2:7-bisdiazonium platinichloride (MORGAN and MICKLETHWAIT), T., 2558; P., 293.
- $C_{10}H_6N_2ClAu$ Naphthalene-2:7-bisdiazonium aurichloride (MORGAN and MICKLETHWAIT), T., 2558; P., 293.
- $C_{10}H_7ONCl$ 2-Chloroquinoline-3-carboxylamide (MILLS and WATSON), T., 754; P., 56.
- $C_{10}H_8O_8N_2S_2$ Naphthalene-2:7-bisdiazonium sulphate ($+\frac{1}{2}EtOH$) (MORGAN and MICKLETHWAIT), T., 2558; P., 293.
- $C_{10}H_{11}O_2NAg$ Silver derivative of α -cyano- β -cyclobutylformylacetic acid (CAMPBELL and THORPE), T., 2424.
- $C_{10}H_{14}O_2NBr$ *d*-Camphorbromimide (EVANS), T., 2238.
- $C_{10}H_{14}O_2NI$ *d*-Camphoriodoimide (EVANS), T., 2239.
- $C_{10}H_{14}O_2NNa$ *d*-Camphorsodioimide (EVANS), T., 2211.
- $C_{10}H_{15}O_2BrS$ *d*-Bromocamphorsulphonic acid, *d*- and *l*-narcotine salts of (FERKIN and ROBINSON), P., 131.
*d**l*- and *l*- α -Bromocamphor- π -sulphonic acid, *d**l*-, and *d*-pavine salts of (POPE and GIBSON), T., 2209.

C₁₁ Group.

- C₁₁H₁₂O: Piperonylideneacetone, isomerides, action of light on (STOBBE and WILSON), T., 1722; P., 206.
- C₁₁H₁₀O: 6-Carboxy-3:4-dimethoxyphenylglyoxylic acid, synthesis of, and distillation of its silver salt (HARDING and WEIZMANN), T., 1129; P., 130.
- C₁₁H₁₀O: 4:6-Dimethyl-*o*-tolylglyoxylic acid (HARDING and WEIZMANN), T., 1128.
- C₁₁H₁₂O: Ethyl *l*- α -hydroxy- α -phenylpropionate (McKENZIE and CLOUGH), T., 3569; P., 325.
- C₁₁H₁₂O: 4:6-Dimethoxy-*o*-methylacetophenone (HARDING and WEIZMANN), T., 1128; P., 130.
- C₁₁H₁₂O: 3:3:5-Dimethoxyphenylpropionic acid (SALWAY), T., 2417.
- C₁₁H₁₆O: Camphorcarboxylic acid, absorption spectra of, and its derivatives (LOWEY, DESCH, and SOUTHGATE), T., 899; P., 68.
- C₁₁H₁₆O: Ethyl α -acetylglutaconate (SIMONSEN), T., 1914.
- C₁₁H₁₆O: Ethyl cyclopentan-1-one-2:5-dicarboxylate (MITCHELL and THORPE), T., 1003.
- C₁₁H₁₆O: α -Diacetonacetin (ALPERN and WEIZMANN), P., 345.
- C₁₁H₁₆O: *l*-Isomenthencarboxylic acid (GARDNER, PERKIN, and WATSON), T., 1770.
- C₁₁H₁₆O: Methyl hydrogen camphorate (EDMINSON and HILDITCH), T., 225.
- C₁₁H₁₆O: Dimethyl- α -thujadicarboxylate (THOMSON), T., 1513; P., 178.
- C₁₁H₁₆O: *l*-Isomentholcarboxylic acid (GARDNER, PERKIN, and WATSON), T., 1771.
- C₁₁H₁₆O: Propyl *l*-methoxysuccinate (PURDIE and NEAYE), T., 1518.
- C₁₁H₁₆O: Ethyl 3-hydroxy-*n*-nonoate (HARDING and WEIZMANN), T., 303.

II III

- C₁₁H₈O₄N₂: 3:5:8-Trinitro-6:7-dimethylcoumarin (CLAYTON), T., 1399.
- C₁₁H₈O₄N₂: 3:6-Dinitro-4:7-dimethylcoumarin (CLAYTON), T., 1398.
- C₁₁H₈O₄N₂: 3:8-Dinitro-6:7-dimethylcoumarin (CLAYTON), T., 1399.
- C₁₁H₈O₄N: 2-Cyano-3-methoxyindene (MITCHELL and THORPE), T., 2278.
- C₁₁H₈O₄N: 6-Nitro-4:7-dimethylcoumarin (CLAYTON), T., 1393.
- C₁₁H₈O₄N: 8-Nitro-5:6-dimethylcoumarin (CLAYTON), T., 1405.
- C₁₁H₈O₄N: 5-Nitro-6:7-dimethylcoumarin (CLAYTON), T., 1398.
- C₁₁H₈O₄N: 6-Nitro-6:7-dimethylcoumarin (CLAYTON), T., 1405.
- C₁₁H₈O₄N₂: 3-Acetylaminquinoline (MILLS and WATSON), T., 753; P., 56.
- C₁₁H₈O₄N₂: Triketohydrindone disemicarbazone (RUHEMANN), T., 1448.
- C₁₁H₈O₄N₂: *m*-Nitrobenzoyl*isobutyronitrile* (DAVIS), T., 951.
- C₁₁H₈O₄N: 6-Amino-4:7-dimethylcoumarin (CLAYTON), T., 1352.
- C₁₁H₈O₄N: 5-Amino-6:7-dimethylcoumarin (CLAYTON), T., 1353.
- C₁₁H₈O₄N: Benzoyloxy*isobutyronitrile* (DAVIS), T., 951; P., 90.
- C₁₁H₈O₄N: Methyl ether of methyl 5-nitrocoumarate (CLAYTON), T., 2108.
- C₁₁H₈O₄N: Methyl ether of methyl 5-nitrocoumarinate (CLAYTON), T., 2107.
- C₁₁H₈O₄N: Ethyl ether of 5-nitrocoumaric acid, and silver salt (CLAYTON), T., 2109.
- C₁₁H₈O₄N: Ethyl ether of 5-nitrocoumarinic acid, and silver salt (CLAYTON), T., 2107.
- C₁₁H₈O₄N: Oxime of 6-carboxy-3:4-dimethoxyphenylglyoxylic acid (HARDING and WEIZMANN), T., 1130.
- C₁₁H₈O₄N₂: 5:8-Diamino-6:7-dimethylcoumarin (CLAYTON), T., 1354.
- C₁₁H₈O₄N₂: 2-Methyl-1-hydrindone semicarbazone (MITCHELL and THORPE), T., 2275.
- C₁₁H₈O₄N: Phenolbetaine of 6:7-dihydroxy-2-ethyl-3:4-dihydroisoquinolinium hydroxide (PYMAN), T., 280.

- $C_{11}H_{13}O_3N$ 7 (or 6)-Hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline, and its sodium salt (PYMAN), T, 271.
6:7-Dihydroxy-1-keto-2-ethyltetrahydroisoquinoline (PYMAN), T, 274.
- $C_{11}H_{13}O_3N$ β -3-Methoxy-4:5-methylenedioxyphenylpropionamide (SALWAY), T, 1211.
- $C_{11}H_{13}O_4N_2$ Ethyl β -imino- α -cyano-1-carboxy- β -cyclobutyl-1-propionate, α - and β -forms of (CAMPELL and THORPE), T, 2422.
- $C_{11}H_{13}ON$ Cyanocarone (CLARKE and LAPWORTH), T, 11.
Substance, from *p*-toluidine and acetaldehyde, α - and β -forms (JONES and WHITE), T, 643; absorption spectra of (FURVIS), T, 646.
- $C_{11}H_{15}ON_3$ Camphane-oxytriazine (FOSTEN and ZIMMERLI), T, 2176.
- $C_{11}H_{15}O_2N$ Acetyl-*p*-hydroxyphenylethylmethylamine (WALPOLEY, T, 943.
- $C_{11}H_{15}O_2N$ Acetyl derivative of 4:5-dimethoxy-*o*-toluidine (LUFF, PUGH, and ROBINSON), T, 1135; P, 132.
 β -3:5-Dimethoxyphenylpropionamide (SALWAY), T, 2417.
6:7-Dihydroxy-2-ethyl-3:4-dihydroisoquinolinium hydroxide, its chloride and picrate (PYMAN), T, 280.
- $C_{11}H_{15}O_3N_2$ 5-Nitro-2-acetyl-amino-dimethyl-*p*-toluidine (MORGAN and CLAYTON), T, 2650; P, 323.
- $C_{11}H_{15}O_3N_2$ α -Formylcamphorquinonehydrazone (FOSTER and ZIMMERLI), T, 2168.
Pilocarpine, constitution of (PYMAN), T, 1814; P, 211.
- $C_{11}H_{17}ON_3$ 2-Acetyl-2:5-diaminodimethyl-*p*-toluidine (MORGAN and CLAYTON), T, 2651; P, 323.
- $C_{11}H_{17}O_2N$ 3:4-Dihydroxyphenylethylpropylamine, and its hydrochloride (PYMAN), T, 275.
Camphorcarboxamide (GLOVER and LOWRY), P, 162.
d-Camphormethylimide, preparation of (EVANS), T, 2232.
Substance, from action of sodium hydroxide on cyanocarone (CLARKE and LAPWORTH), T, 15.
- $C_{11}H_{17}O_3N_2$ Camphorquinone α - and β -semicarbazone (FOSTER and ZIMMERLI), T, 2173; P, 246.
- $C_{11}H_{17}O_4N$ Ethyl 2-imino-*cyclopentane*-1:3-dicarboxylate (MITCHELL and THORPE), T, 1002; P, 114.
- $C_{11}H_{15}O_3S_2$ Camphoryl methyl- β -disulphoxide (HILDITCH), T, 1083; P, 96.
- $C_{11}H_{15}O_4S$ Methyl camphor- β -sulphonate (EDMUNSON and HILDITCH), T, 226.
- $C_{11}H_{13}O_4N_2$ *d*-Camphor-*p*-nitrobenzylimide (EVANS), T, 2241.
- $C_{11}H_{21}O_3N_2$ α -Amino-*n*-nonoylglycine (HOPWOOD and WEIZMANN), P, 70.

11 IV

- $C_{11}H_{11}O_2NCl_3$ Ethyl 2:4:6-trichloromalonanilate (CHATTAWAY and MASON), T, 343.
- $C_{11}H_{11}O_2NBr_3$ Ethyl 2:4:6-tribromomalonanilate (CHATTAWAY and MASON), T, 345.
- $C_{11}H_{11}O_2NCl_2$ Ethyl 2:4-dichloromalonanilate (CHATTAWAY and MASON), T, 342.
- $C_{11}H_{11}O_2NBr_2$ Ethyl 2:4-dibromomalonanilate (CHATTAWAY and MASON), T, 344.
- $C_{11}H_{11}O_4NBr_2$ Methyl $\alpha\beta$ -dibromo-5-nitro-2-methoxy- β -phenylpropionate (CLAYTON), T, 2110.

- $C_8H_7O_2NCl$ Ethyl *p*-chloromalonanilate (CHATTAWAY and MASON), T., 341.
 $C_8H_7O_2NBr$ Ethyl *p*-bromomalonanilate (CHATTAWAY and MASON), T., 341.
 $C_8H_7O_2NCl$ 7 (or 6)-Hydroxy-6 (or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium chloride (PYMAN), T., 278.
 $C_8H_7O_2NI$ 7 (or 6)-Hydroxy-6 (or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium iodide (PYMAN), T., 278.
 $C_8H_7O_2NBr$ Camphocarboxybromoamide (GLOVE and LOWRY), P., 168.
 $C_8H_7O_2NCl$ 3:4-Dihydroxy-8-phenylethyltrimethylammonium chloride (BARGER and EWINS), T., 2258.
 $C_8H_7O_2NBr$ α -Bromo-*n*-nonoylglycine (HORWOOD and WEIZMANN), P., 69.

C_{12} Group.

- $C_{12}H_{10}$ Iodoacenaphthene, and its picrate (CROMPTON and HARRISON), P., 226.
 $C_{12}H_{10}O_2$ 5-Hydroxy-4:6:8-trimethylcoumarin (CLAYTON), T., 1403.
 Ethyl 1-hydrindene-2-carboxylate (MITCHELL and THORPE), T., 2278; P., 245.
 $C_{12}H_{10}O_2$ Hydroxydiacetyldimethoxybenzene (TUTIN and CATON), T., 2065; P., 228.
 $C_{12}H_{10}O_2$ Ethyl 6-methyl-2-pyrone-3:5-dicarboxylate, conversion of, into methylfumaric acid (SIMONSEN), T., 1910; P., 200.
 $C_{12}H_{10}O_2$ 2:3:4-Trimethoxy-8-phenylpropionic acid (BARGER and EWINS), T., 2259.
 $C_{12}H_{10}O_2$ *d*-isoMenthonedicarboxylic acid (GARDNER, PERKIN, and WATSON), T., 1772.
 $C_{12}H_{10}O_2$ Ethyl hydrogen camphorate (EDMONSON and HILDITCH), T., 225.
 Dimethyl-*l*-isocamphorate (SHIBATA), T., 1245.
 $C_{12}H_{10}O_2$ Trimethylfructosemonoacetone (IRVINE and GARRETT), T., 1289.
 $C_{12}H_{10}O_2$ Lauric acid, condensation products of, with glycine, alanine, and leucine (HORWOOD and WEIZMANN), P., 69.

12 III

- $C_{12}H_{10}OS$ Monoxide of diphenylene *p*-disulphide (HILDITCH), T., 2586.
 $C_{12}H_{10}OS$ Diphenylene *p*-disulphoxide (HILDITCH), T., 2585.
 $C_{12}H_{10}OS$ Substance, from oxidation of diphenylene *p*-disulphoxide ($+2H_2O$) (HILDITCH), T., 2588.
 $C_{12}H_7O_5N_3$ 3:5:8-Trinitro-4:6:7-trimethylcoumarin (CLAYTON), T., 1399.
 $C_{12}H_7O_5N_3$ 3:5:8-Trinitro-4:6:8-trimethylcoumarin (CLAYTON), T., 1400.
 $C_{12}H_7O_5N_3$ Substance, from *o*- and *m*-nitroanilines and trinitrobenzene (SUDWORTH and BEARD), T., 783.
 $C_{12}H_7ClN_5$ Benzeneazobenzenediazonium chloride (HEWITT and THOLE), T., 514; P., 54.
 $C_{12}H_7ON$ Substance, from ethyl 1-iminohydrindene-2-carboxylate and nitrous acid (MITCHELL and THORPE), T., 2272.
 $C_{12}H_7ON$ 5:7-Dinitro-4:6:8-trimethylcoumarin (CLAYTON), T., 1400.
 $C_{12}H_7OK$ Potassium compound of ethyl 1-hydrindene-2-carboxylate (MITCHELL and THORPE), T., 2273.
 $C_{12}H_7ON$ 6-Nitro-3:4:7-trimethylcoumarin (CLAYTON), T., 1353.
 $C_{12}H_7ON$ 8-Nitro-4:6:7-trimethylcoumarin (CLAYTON), T., 1399.
 $C_{12}H_7ON$ 5-Nitro-4:6:8-trimethylcoumarin (CLAYTON), T., 1400.
 $C_{12}H_7ON$ 7-Nitro-5:6:8-trimethylcoumarin (CLAYTON), T., 1400.

- $C_{12}H_9O_5N_6$ 5(or 8)-Nitro-6:7-dimethoxy-2-methyl-1:2-dihydroquinolin-11-yl- (PYMAN), T., 270.
- $C_{13}H_{13}O_2N$ 6-Amino-3:4:7-trimethylcoumarin (CLAYTON), T., 1351.
- 6-Amino-4:6:7-trimethylcoumarin (CLAYTON), T., 1353.
- 5-Amino-4:6:8-trimethylcoumarin (CLAYTON), T., 1403.
- 7-Amino-5:6:8-trimethylcoumarin (CLAYTON), T., 1353.
- Ethyl 1-iminohydrindene-2-carboxylate (MITCHELL and THORPE), T., 2271; P., 249.
- $C_{12}H_{13}O_5N$ Methyl ether of ethyl 5-nitrocumarate (CLAYTON), T., 2100.
- Ethyl ether of methyl 5-nitrocumarate (CLAYTON), T., 2100.
- Methyl ether of ethyl 5-nitrocumarinate (CLAYTON), T., 2105.
- Ethyl ether of methyl 5-nitrocumarinate (CLAYTON), T., 2108.
- $C_{12}H_{11}O_3N_2$ 5:7-Diamino-4:6:8-trimethylcoumarin (CLAYTON), T., 1354.
- $C_{12}H_{15}O_4N$ 3-Methoxy-1:1-dimethyl- Δ^2 -cyclohexenylidene-5-cyanoacetate (CROSSLEY and GILLING), T., 530.
- 6:7-Dihydroxy-1-keto-2-propyltetrahydroisoquinoline (PYMAN), T., 270.
- $C_{12}H_{13}O_4N$ Cotarnine, synthesis of, and its aurichloride and picrate (SALWAY), T., 1208; P., 93, 133.
- neo*Cotarnine, and its hydrochloride (+ $1\frac{1}{2}H_2O$), picrate and aurichloride (SALWAY), T., 1217.
- $C_{12}H_{13}NS$ Thiobenzoyl piperidine (RUSSELL), T., 955.
- $C_{12}H_{13}O_2N_2$ Nitroso-derivatives of ethylidenexylidine (JONES and WHITE), T., 642.
- $C_{12}H_{11}ON$ α - and β -Ethylidenexylidine (JONES and WHITE), T., 639; absorption spectra of (PURVIS), T., 647.
- 3-Ethoxy-1:1-dimethyl- Δ^2 -cyclohexenylidene-5-acetonitrile (CROSSLEY and GILLING), T., 531.
- $C_{12}H_{17}O_3N$ Acetyl-*p*-methoxyphenylethylmethylamine (WALFORD), T., 943.
- Ethyl α -cyano-1-methyl- Δ^2 -cyclohexene-3-acetate (HARDING and HAWORTH), T., 494.
- Methyl α -cyano- α -1-methyl- Δ^2 -cyclohexene-2-propionate (HARDING and HAWORTH), T., 496.
- $C_{12}H_{15}O_5N$ Mannoseanilide (IRVINE and McNICOLL), T., 1453.
- $C_{12}H_{15}ON_2$ Oxime of ethylidenexylidine (JONES and WHITE), T., 640.
- $C_{12}H_{15}ON_4$ Cyanocaronesemicarbazide (CLARKE and LAPWORTH), T., 14.
- $C_{12}H_{15}O_2N_2$ α - and β -Acetylcamphorquinonehydrazone (FORSTER and ZIMMERLI), T., 2168.
- $C_{12}H_{15}O_4N_2$ Ethyl β -imino- α' -cyano- $\alpha\alpha'$ -dimethylglutarate, α - and β -forms of (CAMPELL and THORPE), T., 1309; P., 176.
- 2:3:4-Trimethoxy- β -phenylpropionylhydrazide, hydrochloride of (BATHURST and EWINS), T., 2260.
- $C_{12}H_{19}O_2N$ *d*-Camphorethylimide (EVANS), T., 2240.
- $C_{12}H_{21}O_5S$ Ethyl camphor- β -sulphonate (EDMINSON and HILDITCH), T., 24.
- $C_{12}H_{21}O_3N$ Ethyl α -camphoramidic acid (WOOTTON), T., 413.

12 IV

- $C_{12}H_3NCl_4S$ Tetrachlorothiodiphenylamine (PAGE and SMILES), T., 1565.
- Trichlorophenazothionium chloride (+ H_2O) (BRADY and SMILES), T., 1565.
- $C_{12}H_6O_6Br_4$ Substance, from 2:3:4:6-tetrabromoaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.
- $C_{12}H_3O_6N_3Cl_3$ Substance, from *s*-trichloroaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 781.

- $C_6H_3O_2Br_3$ Substance, from 2:4:6-tribromoaniline and trinitrobenzene (SUD-
BOROUGH and BEARD), T., 782.
- C_6H_3ONBr 4-Bromo-2-acetylnaphthylene-1-diazo-2-imide (MORGAN and
GORDEN), T., 1713.
- C_6H_4OClS *p*-Chlorophenol sulphide (GAZDAR and SMILES), T., 2252.
- C_6H_4OClS *o*- and *p*-Chlorophenol sulfoxide (GAZDAR and SMILES), T.,
2251.
- $C_6H_3ONCl_2$ Substance, from 2:4-dichloroaniline and trinitrobenzene (SUD-
BOROUGH and BEARD), T., 781.
- $C_6H_3ONBr_2$ Substance, from 2:4- and 2:6-dibromoaniline and trinitrobenzene
(SUDBOROUGH and BEARD), T., 782.
- C_6H_4NBrS Bromothiodiphenylamine (PAGE and SMILES), T., 1113.
- C_6H_4ONS Phenazothionium hydroxide, intramolecular rearrangement of
the halides of (PAGE and SMILES), T., 1112; P., 133.
- C_6H_4ONS 1-Phenyl-1:2:3-benzotriazole-5-sulphonic acid (SCHWALBE
and WOLFF), P., 340.
- $C_6H_4ONS_2$ Carbazoledisulphonic acid (SCHWALBE and WOLFF), P., 340.
- C_6H_3ONCl Substance, from *o*-, *m*- and *p*-chloroaniline and trinitrobenzene
(SUDBOROUGH and BEARD), T., 781.
- C_6H_3ONBr Substance, from *o*-, *m*- and *p*-bromoaniline and trinitrobenzene
(SUDBOROUGH and BEARD), T., 781.
- $C_6H_4ONS_2$ Aminocarbazoledisulphonic acid (SCHWALBE and WOLFF),
P., 340.
- $C_6H_4ONS_2$ Carbazoledisulphonamide (SCHWALBE and WOLFF), P., 340.
- $C_6H_4ONBr_2$ Methyl α , β -dibromo-5-nitro-2-ethoxy-*S*-phenylpropionate
(CLAYTON), T., 2110.
- $C_6H_4N_2Cl_2Fe$ Hexamethylferrocyanogen chloride (HARTLEY), T., 1720.

12 V

- C_6H_3ONClS Tetrachlorodiphenylamine *o*-sulphoxide (BRADY and
SMILES), T., 1560.
- C_6H_3ONClS Tetrachlorophenazothionium hydroxide (+ H_2O) (BRADY and SMILES),
T., 1562.
- C_6H_3ONClS Trichlorodiphenylamine *o*-sulphoxide, and its hydro-
chloride (BRADY and SMILES), T., 1564.
- C_6H_3ONClS Chlorodinitrodiphenylamine sulphoxide (PAGE and
SMILES), T., 1116.
- C_6H_3ONClS *p*-Chloronitrophenol sulphoxide (GAZDAR and SMILES), T.,
2252.
- $C_6H_3ONClS_2$ Carbazoledisulphonyl chloride (SCHWALBE and WOLFF),
P., 340.
- C_6H_3ONSFe Hexamethylferrocyanogen sulphate (+ $EtOH$) (HART-
LEY), T., 1729.
- $C_6H_3NCl_2FePt$ Platinichloride of substance, from potassium ferro-
cyanide and methyl sulphate (HARTLEY), T., 1072, 1725.
- C_6H_3ONSFe Substance, from potassium ferrocyanide and methyl sulphate
(HARTLEY), T., 1070, 1725.

C_{13} Group.

- $C_{13}H_{10}O$ Substance, from the condensation of cyclobutan-1:3-dione in the
presence of quinoline (CHICK and WILSMORE), T., 1998; P., 217.
- $C_{13}H_{10}N_2$ *p*-Triazobenzaldehydephenylhydrazone (FORSTER and JUDD),
T., 280.

- $C_{12}H_8O_3$ 2:4-Dihydroxybenzhydrol, and its potassium salt (POPE and HOWARD), T., 80.
 $C_{12}H_{10}O_2$ 6:7-Dimethoxy-1-methylnaphthalene (LUFF, PERKIN, and ROBERTSON), T., 1140; P., 133.
 $C_{12}H_8O_6$ Ethyl 2-methyl-1-hydrindone-2-carboxylate (MITCHELL and THORPE), T., 2274.
 $C_{12}H_{14}O_6$ Methyl methyltrimesate (SIMONSEN), T., 1915.
 $C_{12}H_{22}O_2$ Diethylpocampholide (SHIBATA), T., 1242.
 $C_{12}H_{22}O_4$ *n*-Propyl hydrogen camphorate (EDMUNSON and HILDEBRAND), T., 225.
 Diethyl α -thujadicarboxylate (THOMSON), T., 1514; P., 178.

13 III

- $C_{12}H_8OS$ Thioxanthone, new syntheses of (DAVIS and SMILES), T., 1296; P., 93, 174; (SMILES), P., 342.
 $C_{12}H_8O_2S$ Hydroxythioxanthone ($+ \frac{1}{2}H_2O$) (DAVIS and SMILES), T., 1297; P., 174.
 $C_{12}H_{10}ON_2$ *p*-Triazobenzylidene-*p*-aminophenol (FORSTER and JENCKE), T., 260; P., 28.
 $C_{12}H_{10}O_2S$ Diphenylmethane *o*-sulphoxide, intramolecular rearrangement of (HILDITCH and SMILES), P., 174.
 $C_{12}H_{10}O_4N_4$ Substance, from *o*- and *p*-aminobenzoic acid and trinitrobenzene (SUDBOROUGH and BEARD), T., 786.
 $C_{12}H_{12}O_2N_2$ Ethyl α -*o*-dicyano- β -phenylpropionate (MITCHELL and THORPE), T., 2275.
 $C_{12}H_{10}O_4N_4$ Substance, from *o*- and *p*-anisidine and trinitrobenzene (SUDBOROUGH and BEARD), T., 785.
 $C_{12}H_{12}NI$ *N*-Methyldiphenylamine hydriodide, mercuri-iodide of (BARBER and SMILES), T., 984.
 $C_{12}H_8N_2S_2$ Immedial-indone, constitution of (FRANK), T., 2014; P., 218.
 $C_{12}H_{10}O_4N_6$ Substance, from triaminotoluene and trinitrobenzene (SUDBOROUGH and BEARD), T., 787.
 $C_{12}H_{10}O_2N$ α -Benzoyloxyisohexonitrile (DAVIS), T., 951; P., 89.
 $C_{12}H_{12}O_2N_2$ Semicarbazone of ethyl 1-hydrindone-2-carboxylate (MITCHELL and THORPE), T., 2274.
 $C_{12}H_{12}O_4N_2$ Ethyl phenyltriazomalonate (FORSTER and MÜLLER), T., 125; P., 4.
 $C_{12}H_{10}O_3N$ Ethyl ether of ethyl 5-nitrocoumarinate (CLAYTON), T., 255.
 $C_{12}H_{10}O_2N_2$ Ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyridide-5- α -propionate (CAMPELL and THORPE), T., 1314.
 $C_{12}H_{17}O_2N_2$ Acetyl derivative of camphane-oxytriazine (FORMER and ZIMMERLI), T., 2177.
 $C_{12}H_{17}O_3N$ 3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid (CROSSLEY and GILLING), T., 531.
 Ethyl 3-hydroxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid and its silver salt (CROSSLEY and GILLING), T., 527.
 $C_{12}H_{17}O_4N_3$ Ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyridide-5- α -propionate (CAMPELL and THORPE), T., 1313.
 $C_{12}H_{15}O_2N_2$ Ethyl β -imino- α -cyano-1-carbethoxy- α -3-butyl-1-propionate (CAMPELL and THORPE), T., 2422.
 $C_{12}H_{15}ON$ α - and β -isomeride, from ψ -cumidine and acetaldehyde (JONES and WHITE), T., 643.
 $C_{12}H_{16}O_2N$ Gynocardin, and its sodium salt (MOORE and TUTIN), T., 1255; P., 182.
 $C_{12}H_{20}O_2N$ Camphor-*n*-propylimide (WOOTTON), T., 415.

- $C_9H_9O_2N$ Allyl- α -camphoramic acid (WOOTTON), T., 413.
 $C_9H_9O_2N$ α -Propyl- α -camphoramic acid (WOOTTON), T., 413.

13 IV

- $C_9H_8O_2NS$ Dinitro- N -methylphenazothionium hydrate (BARNETT and SMILES), T., 191.
 $C_9H_8ON_2K$ Substance, from potassium *o*-, *m*-, and *p*-aminobenzoate and tri-nitrobenzene (SUDBOROUGH and BEARD), T., 786.
 $C_9H_8O_2NS_2$ Methanedisulphonylbis-*p*-phenylenediazoimide (MORGAN, PICKARD, and MICKLETHWAIT), T., 60.
 C_9H_8NCIS Chloro- N -methylthiodiphenylamine (PAGE and SMILES), T., 1116.
 C_9H_8ONS N -Methyldiphenylamine *o*-sulphoxide (BARNETT and SMILES), T., 188.
 N -Methylphenazothionium, platinumchloride of (BARNETT and SMILES), T., 189.
 C_9H_8ONS Toluene-*o*-sulphonyl-*p*-phenylenediazoimide (MORGAN and PICKARD), T., 57.
 C_9H_8ONS Toluene-*o*-sulphonyl-*p*-nitroaniline (MORGAN and PICKARD), T., 56.
 $C_9H_8ONS_2$ Methanedisulphonylbis-*p*-nitroaniline (MORGAN, PICKARD, and MICKLETHWAIT), T., 58.
 $C_9H_8ON_2S_2$ Methanedisulphonylbis-*p*-aminobenzenediazonium nitrate (MORGAN, PICKARD, and MICKLETHWAIT), T., 58.
 C_9H_8NIS S -Methyldiphenylamine-*o*-sulphonium iodide, mercuri-iodide of (BARNETT and SMILES), T., 983.
 C_9H_8ONS S -Methylphenazothionium hydroxide, hydrochloride and platinumchloride of (BARNETT and SMILES), T., 986.
 C_9H_8ONS Toluene-*o*-sulphonyl-*p*-phenylenediamine (MORGAN and PICKARD), T., 56.
 C_9H_8ONAg Silver compound of ethyl 4-cyano-2-keto-4-carbethoxy-tetrahydropyrrolidene-5- α -propionate (CAMPELL and THORPE), T., 1314.
 C_9H_8ONK Potassium compound of ethyl 4-cyano-2-keto-4-carbethoxy-tetrahydropyrrolidene-5- α -propionate (CAMPELL and THORPE), T., 1314.
 $C_9H_8ON_2S_2$ Methanedisulphonylbis-*p*-phenylenediamine (MORGAN, PICKARD, and MICKLETHWAIT), T., 58.

13 V

- $C_9H_8ON_2CIS$ Chlorodinitro- N -methyldiphenylamine *o*-sulphoxide (PAGE and SMILES), T., 1117.
 $C_9H_8ON_2Cl_2S_2$ Methanedisulphonylbis-*p*-aminobenzenediazonium chloride (MORGAN, PICKARD, and MICKLETHWAIT), T., 58.

C_{14} Group.

- $C_{14}H_8$ Tetramethyl-naphthalene, absorption spectrum of (HOMER and FRAVIS), T., ...; T., 5.

14 II

- $C_{14}H_6Cl_4$ 3:4:8:4'-Tetrachlorotoluene tetrachloride (KENNER and WITAM), T., 1364.
 $C_{14}H_6O_2$ Phenanthraquinone, condensations of, with ethyl malonate and ethyl acetoacetate (RICHARDS), T., 1456; P., 195.

XXVII.

- $C_{14}H_8Cl_2$ 4:4'-Dichlorotolane (KENNER and WITHAM), T., 1965; P., 219.
 $C_{14}H_8Cl_2$ *cis*- and *trans*-4:4'-Dichlorotolane dichloride (KENNER and WITHAM), T., 1964; P., 219.
 $C_{14}H_8Cl_4$ 4:4'-Dichlorotolane tetrachloride (KENNER and WITHAM), T., 1963; P., 219.
 $C_{14}H_{12}O_2$ Benzoin, substituted indoles from (RICHARDS), T., 977; P., 92.
 l -Benzoin, optically active glycols from (McKENZIE and WREN), T., 473; P., 54.
 $C_{14}H_{12}O_5$ Substance, from red clover flowers (POWER and SALWAY), T., 243; P., 20.
 $C_{14}H_{14}O_4$ 2:4-Dihydroxy-4'-methoxybenzhydrol, and its dipotassium salt (POPE and HOWARD), T., 972; P., 83.
 $C_{14}H_{14}O_5$ Methyl mellophanate (BAMFORD and SIMONSEN), T., 1909.
 $C_{14}H_{14}S_2$ Benzyl disulphide (SMYTHE and FORSTER), T., 1196.
 $C_{14}H_{14}S_3$ Benzyl trisulphide, and its additive compound with silver nitrate (SMYTHE and FORSTER), T., 1196; P., 135.
 $C_{14}H_{14}S_4$ Benzyl tetrasulphide (SMYTHE and FORSTER), T., 1198; P., 136.
 $C_{14}H_{13}N$ α -Phenyl- Δ^1 -cyclohexene-1-acetonitrile (HARDING and HAWORTH), T., 497.
 $C_{14}H_{16}O_3$ Piperonylidene-pinacolone (BOON and WILSON), T., 1753; P., 203.
 $C_{14}H_{16}O_6$ Acetoxydiacetyl dimethoxybenzene (TUTIN and CATON), T., 2066.
 $C_{14}H_{20}O_5$ Ethyl 2:3:4-trimethoxy- β -phenylpropionate (BARGER and EWING), T., 2250.
 $C_{14}H_{20}O$ 1:4'-Dimethyl-3-cyclohexylidene-cyclohexan-4-one (LUFF and PERKIN), T., 2155.
 $C_{14}H_{22}O_2$ Diethylcampholide (SHIBATA), T., 1241.
 $C_{14}H_{22}O_4$ Methyl 1:2:3-trimethyl-3-isobutyl- γ -cyclopentane-1-carboxylate (SHIBATA), T., 1244; P., 142.
 $C_{14}H_{24}O_4$ *n*-Butyl hydrogen camphorate (EDMINSON and HILDITCH), T., 226.
 $C_{14}H_{24}O_6$ Ethyl pentane- $\alpha\beta\gamma$ -tricarboxylate (HOPE and PERKIN), P., 178.
 Ethyl isopentane- $\alpha\beta\gamma$ -tricarboxylate (HOPE and PERKIN), P., 179.

14 III

- $C_{14}H_8O_2Cl_2$ 1:4-Dichloroanthraquinone (WALSH and WEIZMANN), T., 651; P., 61.
 $C_{14}H_8O_2Cl_2$ 4:4'-Dichlorobenzil (KENNER and WITHAM), T., 1967.
 $C_{14}H_8O_2N$ 2-Phenyl-1:3-benzoxazine-4-one (TITHERLEY), T., 200; P., 9.
 $C_{14}H_{10}OS$ Methylthioxanthone (DAVIS and SMILES), T., 1297; P., 174.
 $C_{14}H_{12}O_2N_4$ Benzoyl derivative of *p*-triazobenz-*anti*-aldoxime (FORSTER and JUDD), T., 259.
 $C_{14}H_{10}OS$ Methoxythioxanthone (DAVIS and SMILES), T., 1297; P., 174.
 $C_{14}H_{10}O_2S_2$ Di-*o*-carboxyphenyl disulphoxide (HILDITCH), T., 2591.
 $C_{14}H_{12}O_2N$ Dibenzamide, action of phosphorus pentachloride on (TITHERLEY and WORRELL), T., 839; P., 93.
 $C_{14}H_{12}O_2S_2$ Ditolylene *p*-disulphoxide (HILDITCH), T., 2591.
 $C_{14}H_{12}O_2N_4$ Substance, from *p*-aminoacetophenone and trinitrobenzene (SUDBOROUGH and BEARD), T., 786.
 $C_{14}H_{12}O_2N_4$ Substance, from methyl *o*- and *p*-aminobenzoate and trinitrobenzene (SUDBOROUGH and BEARD), T., 785.
 $C_{14}H_{12}N_2Br$ Triazooacetophenonebromophenylhydrazine (FORSTER and MÜLLER), T., 141.

- $C_6H_5ON_2$ *o*-, *m*-, and *p*-Nitrobenzeneazophenetole (BALY, TUCK, and MURSDEN), T., 1501.
 $C_6H_5ON_2$ 2-Nitro-4'-acetylbenzidine (CAIN and MAY), T., 725.
 $C_6H_5ON_2$ Phenylhydrazone of 5-nitro-4-methylsalicylaldehyde (CLAYTON), T., 1407.
 C_6H_5OS *p*-Cresol sulphide (GAZDAR and SMILES), T., 2250.
 C_6H_5OS *p*-Cresol *m*-sulphoxide (GAZDAR and SMILES), T., 2248.
 $C_6H_5ON_2$ Substance, from ethyl 1-cyanocyclopropane-1-carboxylate (MITCHELL and THORPE), T., 1001.
 C_6H_5ON Ethyl *o*-cyano- α -benzylacetoacetate (MITCHELL and THORPE), T., 2278.
 C_6H_5OBr Piperonylidene-pipacoline monobromide (BOON and WILSON), T., 1753; P., 208.
 $C_6H_5OBr_2$ Piperonylidene-pipacoline dibromide (BOON and WILSON), T., 1754; P., 208.
 C_6H_5ON Oxime of piperonylidene-pipacoline (BOON and WILSON), T., 1756; P., 208.
 $C_6H_5ON_2$ Semicarbazone of ethyl 2-methyl-1-hydrindone-2-carboxylate (MITCHELL and THORPE), T., 2275.
 $C_6H_5ON_2$ Ethyl 4-cyano-2-keto-4-carbethoxy-1-methyltetrahydropyridylidene-5- α -propionate (CAMPELL and THORPE), T., 1315.
 C_6H_5ON Ethyl 3-methoxy-1:1-dimethyl- Δ^4 -cyclohexenylidene-5-cyanoacetate, two stereoisomides (CROSSLEY and GILLING), T., 528.
 C_6H_5ON Oxime of 1:4'-dimethyl-3-cyclohexylidene-cyclohexan-4-one (LUFF and PERKIN), T., 2156.
 $C_{10}H_{16}ON$ Camphor- α -butylimide (WOOTTON), T., 415.
 $C_{10}H_{16}OS_2$ Camphoryl α -butyl- β -disulphoxide (HILDITCH), T., 1098; P., 26.
 $C_{10}H_{16}ON$ Carpaine, constitution of (BARGER), T., 466; P., 53.
 $C_{10}H_{16}ON$ α -Butyl- α -camphoramie acid (WOOTTON), T., 413.
 $C_{10}H_{16}ON$ Carpamie acid, and its hydrochloride (BARGER), T., 469; P., 53.

14 IV

- $C_{14}H_9O_2Cl_2$ 1:4-Dichloro-5-nitroanthraquinone (WALSH and WEIZMANN), T., 687.
 $C_{14}H_9O_2ClS$ 1:4-Dichloroanthraquinone-6-sulphonic acid, sodium salt of (WALSH and WEIZMANN), T., 688.
 $C_{14}H_9O_2Cl_2$ 1:4-Dichloro-5-aminoanthraquinone (WALSH and WEIZMANN), T., 687.
 $C_{14}H_9ONCl$ 6-Chloro-2-phenyl-1:3-benzoxazine-4-one (TITHERLEY and HUGHES), T., 1376; P., 175.
 $C_{14}H_9ONBr$ 6-Bromo-2-phenyl-1:3-benzoxazine-4-one (HUGHES and TITHERLEY), P., 344.
 $C_{14}H_9ONCl$ α -Chloro-*N*-benzoylbenzamide, preparation of, from dibenzamide (TITHERLEY and WERRALL), T., 840; P., 93.
 $C_{14}H_9ONCl$ *syn*-Benzylidene-5-chlorosalicylamide (TITHERLEY and HUGHES), T., 1376; P., 175.
 $C_{14}H_9ONCl$ 6-Chloro-2-phenyldihydro-1:3-benzoxazine-4-one (TITHERLEY and HUGHES), T., 1374; P., 175.
 $C_{14}H_9ONBr$ *syn*-Benzylidene-5-bromosalicylamide (HUGHES and TITHERLEY), P., 344.
 $C_{14}H_9ONBr$ 6-Bromo-2-phenyldihydro-1:3-benzoxazine-4-one (HUGHES and TITHERLEY), P., 344.
 $C_{14}H_9ONCl$ α - and N -Benzoyl-5-chlorosalicylamide (TITHERLEY and HUGHES), T., 1380; P., 175.

- $C_{14}H_{10}O_2NBr$ *O*-Benzoyl-5-bromosalicylamide (HUGHES and TITHERLEY, P., 344.
N-Benzoyl-5-bromosalicylamide (HUGHES and TITHERLEY), P., 344.
 $C_{14}H_{11}O_2NS_2$ Dicarboxybenzenesulphohydroxamic acid (DAVIS and SMILES), T., 1295.
 $C_{17}H_{15}ONCl$ Diphenylethloroacetamide (CLARKE), T., 429.
 $C_{14}H_{12}ON_2Cl_2$ 2:2' and 3:3'-Dichloroacetylbenzidine (CAIN and MAY), T., 723.
 $C_{11}H_{12}O_2N_2S$ Nitro-*p*-cresol sulphide (GAZDAR and SMILES), T., 2251.
 $C_{11}H_{12}O_2N_2S$ Nitro-*p*-cresol sulphoxide (GAZDAR and SMILES), T., 2250.
 $C_{17}H_{14}NIS$ *N*-*S*-Dimethyldiphenylamine-*o*-sulphonium iodide, mercuric iodide of (BARNETT and SMILES), T., 985.
 $C_{11}H_{15}O_2N_2S$ *p*-Dimethylaminoazobenzene-*p*-sulphonic acid, sodium salt. (methyl orange) colour changes of, in acid solution (TIZARD), T., 2477; P., 225.
 $C_{14}H_{22}O_2NCl_2$ Substance, from carpine hydrochlorids and chlorine (BARGER, T., 472; P., 53.

14 V

- $C_{11}H_{22}O_4N_2S_2Fe$ Hexamethyl ferrocyanogen methyl sulphate (HARTLEY, T., 1726; P., 210.

C₁₅ Group.

- $C_{15}H_{10}O_2$ Substance, from red clover flowers (POWER and SALWAY), T., 239; P., 20.
 $C_{15}H_{12}O_5$ Eriodictyol (2:4:6-trihydroxyphenyl 3:4-dihydroxyethyl ether) (TUTIN), T., 2058; P., 222.
 $C_{15}H_{16}O_2$ 1- α :3-Dihydroxy- α : β -diphenylpropane (MCKENZIE and WREN, T., 477.
 $C_{15}H_{16}O_3$ 2:4-Dimethoxybenzhydrol (POPE and HOWARD), T., 81.
 $C_{15}H_{17}N$ α -Phenyl-1-methyl- Δ^3 -cyclohexene-4-acetonitrile (HARDING and HAWORTH), T., 498.
 $C_{15}H_{26}O_4$ Di-*n*-propyl α -thujadicarboxylate (THOMSON), T., 1514; P., 178.
 $C_{15}H_{26}N_2$ Substance, from ethylenexylidine and phenylbenzylhydrazine (JONES and WHITE), T., 641.

15 III

- $C_{15}H_8ON_2$ Ketohydrindenophenazine (RUHEMANN), T., 1449.
 $C_{15}H_8O_2Cl_2$ 1:4-Dichloro-8-hydroxy-5-methylantraquinone (WALSH and WEIZMANN), T., 690.
 1:4-Dichloro-6 (or 5-) -hydroxy-5 (or 6-) -methylantraquinone (WALSH and WEIZMANN), T., 691.
 $C_{15}H_{10}O_2N_4$ 5-*p*-Nitrobenzeneazo-8-hydroxyquinoline, and its hydrochloride and sodium salt (FOX), T., 1343.
 $C_{15}H_{10}O_2Cl_2$ 3:6-Dichloro-5' (or 6') -hydroxy-2-*o* (or *m*-) -toluylbenzoic acid, and its sodium salt (WALSH and WEIZMANN), T., 689.
 3:6-Dichloro-3' (or 2') -hydroxy-2-*o* (or *m*-) -toluylbenzoic acid (WALSH and WEIZMANN), T., 691.
 $C_{15}H_{10}O_2N_4$ Substance, from quinoline and trinitrobenzene (SCUDBOROUGH and BEARD), T., 794.
 Substance, from isquinoline and trinitrobenzene (SCUDBOROUGH and BEARD), T., 795.
 $C_{15}H_{11}ON_2$ Quinolineazophenol, and its hydrochlorides (FOX), T., 1346.
 5-Benzenediazo-8-hydroxyquinoline, and its salts, (FOX), T., 1339; P., 157.
 $C_{15}H_{11}O_2N$ ω -Amino- α -hydroxy-acetophenone, hydriodide (TUTIN), T., 2513; P., 245.

- $C_8H_5O_2N_2$ Substance, from 3-phenylpyrazolone and trinitrobenzene (SUDBOROUGH and BEARD), T., 797.
- $C_8H_5ON_4$ 5-*p*-Aminobenzeneazo-8-hydroxyquinoline, and its salts (Fox), T., 1343.
- $C_8H_5O_2N_2$ Substance, from α -methylindole and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.
- C_8H_5ON α -Benzoylamino-*op*-dihydroxyacetophenone (TUTIN), T., 2516.
- $C_8H_5O_2N_4$ Substance, from tetrahydroquinoline and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.
- $C_8H_5O_2N_2$ Substance, from trinitrobenzene and dimethyl-*p*-aminobenzaldehyde (SUDBOROUGH and BEARD), T., 791.
- $C_8H_5O_2N_4$ Substance, from ethyl *o*- and *p*-aminobenzoate and trinitrobenzene (SUDBOROUGH and BEARD), T., 785.
- $C_8H_5O_2N_2$ Dimethylaminoazobenzene-*o*-carboxylic acid (*methyl red*), colour changes of, in acid solution (TIZARD), T., 2477; P., 225.
- $C_8H_5O_2N_2$ Substance, from acetonephenylhydrazone and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.
- C_8H_5NS Phenylethylthiobenzamide (RUSSELL), T., 957.
- C_8H_5ON Benzenesulphonyl-*p*-methoxyphenylethylamine (WALPOLE), T., 946.
- Benzoyloscine, resolution of (TUTIN), T., 1793; P., 215.
- Benzoyl-*l*-oscine, and its salts (TUTIN), T., 1796; P., 215.
- C_8H_5ON Ethyl *o*-cyanobenzylmalonate (MITCHELL and THORPE), T., 2270; P., 249.
- C_8H_5ON α -Benzoyloxyoctonitrile (DAVIS), T., 951; P., 89.
- C_8H_5ON 3-*t*-Diacetoxy-*N*-acetylphenylethylmethylamine (PYMAN), T., 278.
- C_8H_5ON Ethyl 3-ethoxy-1:1-dimethyl- Δ^2 -cyclohexenylidene-5-cyanoacetate, two stereoisomerides (CROSSLEY and GILLING), T., 529.
- C_8H_5ON Trimethylrhannoseanilide (IRVINE and McNICOLL), T., 1455.
- C_8H_5ON Ethyl β -cyanopentane- $\alpha\beta$ -tricarboxylate (HOPE and PERKIN), P., 178.
- Ethyl β -cyanopentane- $\alpha\beta$ -tricarboxylate (HOPE and PERKIN), P., 178.
- C_8H_5ON Camphor-*n*-amylimide (WOOTTON), T., 415.
- C_8H_5ON *n*-Amyl- α -camphoramie acid (WOOTTON), T., 413.

15 IV

- $2,4,6,2':4':6'$ -Hexachloromalonanilide (CHATTAWAY and MASON), T., 342.
- $2,4,6,2':4':6'$ -Hexabromomalonanilide (CHATTAWAY and MASON), T., 344.
- $2,4,6,2':4':6'$ -Dichlorobromo-5' (or 6')-hydroxy-2-*o* (or *m*)-toluoylbenzoic acid (WALSH and WEIZMANN), T., 689.
- H_5ON_2Br 5-*p*-Bromobenzeneazo-8-hydroxyquinoline, and its hydrochlorides (Fox), T., 1342.
- $H_5ON_2Cl_4$ 2:4:2':4'-Tetrachloromalonanilide (CHATTAWAY and MASON), T., 342.
- $H_5ON_2Br_4$ 2:4:2':4'-Tetrabromomalonanilide (CHATTAWAY and MASON), T., 344.
- $H_5ON_2Cl_2$ *pp*-Dichloromalonanilide (CHATTAWAY and MASON), T., 340.
- $H_5ON_2Br_2$ *pp*-Dibromomalonanilide (CHATTAWAY and MASON), T., 343.
- H_5ON_2S Phenetoleazobenzaldehydesulphonic acid, metallic salts of, (GREEN and SEN), T., 2243.
- H_5ON_2S Benzenesulphonyl-*p*-hydroxyphenylethylmethylamine (WALPOLE), T., 947.

C₁₆ Group.

- C₁₆H₁₀O₂** 2-Keto-4:5-diphenylene-2:3-dihydrofuran (RICHARDS), T., 1458; P., 195.
- C₁₆H₁₀O₆** Trifolitin (POWER and SALWAY), T., 240; P., 20.
- C₁₆H₁₀O₇** Substance, from red clover flowers (POWER and SALWAY), T., 236; P., 20.
- C₁₆H₁₂O** 3-Phenyl-1-naphthol (RUEHMANN), T., 461.
- C₁₆H₁₂O₃** 9-Hydroxy-10-phenanthrylacetic acid, and its barium and sodium salts (RICHARDS), T., 1458; P., 195.
- C₁₆H₁₂O₄** Pratol, from red clover flowers (POWER and SALWAY), T., 233; P., 20.
- C₁₆H₁₂O₆** Dura-santalin (PERKIN), T., 223; P., 23.
- C₁₆H₁₂O₇** *iso*Rhamnetin, in red clover flowers (POWER and SALWAY), T., 244; P., 20.
- C₁₆H₁₂N₂** 2:5-Diphenylpyrazine, salts of (TUTIN and CATON), T., 2530; P., 245.
- 2:6-Diphenylpyrazine, salts of (TUTIN), T., 2501; (TUTIN and CATON), T., 2531; P., 245.
- C₁₆H₁₂N₂** Phenylhydrazone of 2-cyano-1-hydrindone (MITCHELL and THORPE), T., 2273.
- C₁₆H₁₄O₂** β -Benzyleinnamic acid (RUEHMANN), T., 460.
- Phenyl *o*-methoxystyryl ketone (*o*-methoxybenzylidenacetophenone) (STORER and WILSON), T., 1724; P., 205.
- C₁₆H₁₄O₃** Benzoyl derivative of methyl *p*-coumarate (POWER and SALWAY), T., 235.
- C₁₆H₁₄O₄** Homoeriodietyl (2:4:6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone) (TUTIN), T., 2059; P., 222.
- Hesperitin (2:4:6-trihydroxyphenyl β -hydroxy-4-methoxystyryl ketone) (TUTIN), T., 2060; P., 222.
- Monomethyleiriodietyl (2:6-dihydroxy-4-methoxyphenyl 3:4-dihydroxyphenyl ketone) (TUTIN), T., 2059.
- C₁₆H₁₆O₂** β -Phenyl- β -benzylpropionic acid, and its silver salt (RUEHMANN), T., 460.
- C₁₆H₁₆N₂** Phenylhydrazone of 2-methyl-1-hydrindone (MITCHELL and THORPE), T., 2275.
- C₁₆H₁₆O₂** Dimethoxy-*p*-tolylphenylmethane (MACKENZIE), P., 170.
- l*- α -8-Dihydroxy- α -8-diphenylbutane (MCKENZIE and WREN), T., 479.
- C₁₆H₁₆O₆** Ethyl methyltrimesate (SIMONSEN), T., 1913.
- C₁₆H₁₆O₄** Phenyl hydrogen camphorate (EDMONSON and HILDITCH), T., 225.
- α - and β -Etoxyypiperonylideneepinacolone (BOON and WILSON), T., 1755; P., 208.
- Benzyl α -thujadicarboxylate (THOMSON), T., 1515; P., 178.

16 III

- C₁₆H₁₀O₂N₂** Indirubin (BLOXAM and PERKIN), T., 1460; P., 168.
- C₁₆H₁₀O₂Cl₂** 1:4-Dichloro-7 (or 5)-methoxy-5 (or 7)-methylantraquinone (WALSH and WEIZMANN), T., 692.
- C₁₆H₁₁O₂N** ω -Phthalimino-*op*-dihydroxyacetophenone (TUTIN), T., 2617.
- C₁₆H₁₁O₂N₅** Substance, from β -imino- α -cyanohydrindene and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.
- C₁₆H₁₁O₂N₆** Substance, from α -nitro- β -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 785.
- C₁₆H₁₂O₂N₂** *oo'*-Dihydroxy-2:5-diphenylpyrazine (TUTIN), T., 2518; P., 245.
- pp'*-Dihydroxy-2:6-diphenylpyrazine, and its salts (TUTIN), T., 2523; P., 244.

- $C_8H_5O_2N_2$ Substance, from triketohydrindene and benzamidine (RUEHMANN), T., 2629; P., 235.
- $C_8H_5O_2N_2$, *oo'pp'*-Tetrahydroxy-2:5-diphenylpyrazine, and its sulphates (TUTIN), T., 2514; P., 245.
- $C_8H_5O_2Cl_2$, 3:6-Dichloro-4' (or 2')-methoxy-2-o (or *p*)-tolnoylbenzoic acid (WALSH and WEIZMANN), T., 691.
- $C_8H_5ON_2$, 5-*p*-Tolueneazo-8-hydroxyquinoline, and its salts (FOX), T., 1311.
- C_8H_5ON 1-Hydrindone-2-carbanilide (MITCHELL and THORPE), T., 2274.
- C_8H_5ON ω -Phthalamino-*op*-dihydroxyacetophenone, (TUTIN), T., 2517.
- $C_8H_5ON_2$ Substance, from *o*-amino-*p*-toluquinone and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.
- Substance, from trinitrobenzene and naphthylenediamine (1:2, 1:4, 1-5, and 1-8) (SUDBOROUGH and BEARD), T., 787.
- $C_8H_5ON_2$ Substance, from 1-phenyl-3-methylpyrazolone and trinitrobenzene (SUDBOROUGH and BEARD), T., 797.
- $C_8H_5O_2N_2$, 2:2'-Dinitrodiacetylbenzidine (CAIN and MAY), T., 724.
- C_8H_5ON Diphenacylamine, hydriodide of (TUTIN), T., 2521; P., 244.
- $C_8H_5ON_2$, *pp'*-Dihydroxydiphenacylamine, and its salts (TUTIN), T., 2522; P., 244.
- $C_8H_5O_2N_2$, 2-Nitrodiacetylbenzidine (CAIN and MAY), T., 725.
- C_8H_5ON *mm'pp'*-Tetrahydroxydiphenacylamine, salts of (TUTIN), T., 2523; P., 244.
- $C_8H_5ON_2$ Substance, from *ar*-tetrahydro- α -naphthylamine (SUDBOROUGH and BEARD), T., 736.
- $C_8H_5O_2N_3$ Caffeine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 453.
- C_8H_5ON Nareissine and its hydrochloride (EWINS), T., 2406; P., 296.
- $C_8H_5O_2N_2$, 4'-Acetyl-3-ethoxybenzidine (CAIN and MAY), T., 725.
- $C_8H_5O_2N_2$, *p*-Azoxyphenetole, absorption of carbon dioxide by, relation between solubility and the physical state of the solvent in the (HOMFRAY), T., 1669; P., 197.
- Acetyldianisidine (and + H_2O) (CAIN and MAY), T., 723.
- $C_8H_5ON_2$ Camphor-3-nitrophenylimide (WOOTTON), T., 415.
- C_8H_5ON Laurepukine (ASTON), T., 1387; P., 11.
- $C_8H_5O_2N_2$ Substance, from tetramethyl-*p*-phenylenediamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 792.
- C_8H_5ClSi Dibenzylethylsiliclyl chloride (CHALLENGER and KIPPING), T., 146.
- $C_8H_5O_2S$ Phenyl camphor- β -sulphonate (EDMUNSON and HILDITCH), T., 228.
- $C_8H_5O_2N_2$, 3-Nitrophenyl- α -camphoramie acid (WOOTTON), T., 413.
- C_8H_5ON 4-Hydroxyphenyl- α -camphoramie acid (WOOTTON), T., 414.
- $C_8H_5O_2Br$ Bromoethoxypiperonylideneapinaeolin (BOON and WILSON), T., 1751.
- $C_8H_5ON_2$, 3-Aminophenyl- α -camphoramie acid, and its hydrochloride (WOOTTON), T., 414.
- C_8H_5ON Δ^2 -Noreno-*p*-tolnide (HARDING and WEIZMANN), T., 302.
- $C_8H_5O_2N$ Camphorecarboxypiperidide (GLOVER and LOWRY), P., 163.
- C_8H_5ON Tetramethyl mannoseanilide (IRVINE and McNICOLL), T., 1452.
- Tetramethyl galactoseanilide (IRVINE and McNICOLL), T., 1451.
- C_8H_5ON Camphor-*n*-hexylimide (WOOTTON), T., 415.
- $C_8H_5O_2N_2$ *n*-Hexyl- α -camphoramie acid (WOOTTON), T., 413.
- $C_8H_5O_2N$ Ethyl carpamate, hydrochloride of (BARGER), T., 469.

16 IV

- $C_{16}H_9O_3NCl_2$ 1:4-Dichloro-5-acetylaminoanthraquinone (WALSH and WEIZMANN), T., 688.
- $C_{16}H_2O_2N_4S_2$ Dinitro-8-thienylphenazothionium hydroxide ($+ \frac{1}{2}H_2O$) (BARNETT and SMILES), T., 373.
- $C_{16}H_{15}O_2N_4Br_2$ Substance, from 1:6-dibromo-2-naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.
- $C_{16}H_{11}O_2N_4S$ 1-Benzenesulphonylnaphthylene-2-diazo-1-imide (MORGAN and GODDEN), T., 1717.
- 2-Benzenesulphonylnaphthylene-1-diazo-2-imide (MORGAN and GODDEN), T., 1715.
- Benzenesulphonylnaphthylene-2:3-diazoimide (MORGAN and GODDEN), T., 1718.
- $C_{16}H_{11}O_2NCl_2$ 1:4-Dichloro-5-aminoanthraquinone acetate (WALSH and WEIZMANN), T., 688.
- $C_{16}H_{11}O_2N_2S$ Benzenesulphonyl-2:4-dinitro- α -naphthylamine (MORGAN and GODDEN), T., 1715.
- $C_{16}H_{11}O_2N_4Br$ Substance, from 4-bromo-1-naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.
- Substance, from α -bromo- β -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.
- $C_{16}H_{12}O_4N_2S$ Benzenesulphonyl-1-nitro- β -naphthylamine (MORGAN and GODDEN), T., 1714.
- $C_{16}H_{14}O_2N_2Cl_2$ 2:2'-Dichlorodiacylbenzidine (CAIN and MAY), T., 724.
- $C_{16}H_{12}O_2N_2S$ 2-Benzenesulphonyl-1:2-naphthylenediamine (MORGAN and GODDEN), T., 1714.
- $C_{16}H_{12}O_2N_2Cl_2$ Tartarodi-*o*, *m*, and *p*-chloroanilide (FRANKLAND and TWISS), T., 159.
- $C_{16}H_{12}O_2N_2Br_2$ Tartarodi-*o*, *m*, and *p*-bromoanilide (FRANKLAND and TWISS), T., 157.
- $C_{16}H_{12}O_2N_4S$ 1-Benzenesulphonyl-1:2:4-triaminonaphthalene (MORGAN and GODDEN), T., 1716.
- $C_{16}H_{15}O_2NCl$ Phenylurethane of γ -chloro- β -hydroxy- α -phenoxypropane (BOYD and MARLE), T., 1789; P., 209.
- $C_{16}H_{13}O_2NCl$ Camphor-2-, 3-, and 4-chlorophenylimide (WOOTTON), T., 415.
- $C_{16}H_{13}O_2NBr$ Camphor-2-, and 3-bromophenylimide (WOOTTON), T., 415.
- $C_{16}H_{20}O_2NCl$ 2-, 3-, and 4-Chlorophenyl- α -camphoramic acid (WOOTTON), T., 415.
- $C_{16}H_{20}O_2NBr$ 2-, and 3-Bromophenyl- α -camphoramic acid (WOOTTON), T., 415.
- $C_{16}H_{22}O_2NBr$ Camphorcarboxybromopiperidine (GLOVER and LOWRY), P., 163.

16 V

- $C_{16}H_9O_2N_4BrS$ 2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (MORGAN and GODDEN), T., 165.
- 1-Benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide (MORGAN and GODDEN), T., 1712; P., 165.
- $C_{16}H_{11}O_2N_4BrS$ Benzenesulphonyl-2-nitro-4-bromo- α -naphthylamine (MORGAN and GODDEN), T., 1711.
- $C_{16}H_{12}O_2NBrS$ Benzenesulphonyl-4-bromo- α -naphthylamine (MORGAN and GODDEN), T., 1710.
- $C_{16}H_{13}O_2N_2BrS$ 1-, and 2-Benzenesulphonyl-4-bromo-1:2-naphthylenediamine (MORGAN and GODDEN), T., 1709; P., 165.
- $C_{16}H_{22}O_2N_6S_2Fe$ Substance, from potassium ferrocyanide and methyl sulphate (HARTLEY), T., 1071, 1725.

C₁₇ Group.

- C₁₇H₁₀O. 2-Benzo- α -naphthol, and its salts (EDMUNSON and HILDITCH), T., 226.
 C₁₇H₁₀O. Pratensol, from red clover flowers (POWER and SALWAY), T., 238; P., 20.
 C₁₇H₁₀N₄. 3-*p*-Tolyl- β -naphthaisotriazole (2-*p*-tolyl-naphthylene-1-diazo-2-imine), (MORGAN and BRAMLEY), P., 151.
 C₁₇H₁₄O. Chrysophanic acid dimethylether (TUTIN and CLEWER), T., 6.
 C₁₇H₁₄O₂. $\beta\beta$ -Dibenzoylpropane (SMEDLEY), T., 1492.
 C₁₇H₁₆O₂. 2,4-Diacetoxylbenzhydrol (POPE and HOWARD), T., 80.
 C₁₇H₁₈O. Triethyl hydrogen prehnitate (BAMFORD and SIMONSEN), T., 1908.
 C₁₇H₁₈O₂. Menthyl benzoate (COHEN and DUDLEY), T., 1750.
 C₁₇H₂₀O₂. Diisobutyl α -thujadicarboxylate (THOMSON), T., 1514; P., 178.

17 III

- C₁₇H₁₀OS. Naphthathioxanthone (DAVIS and SMILES), T., 1298; P., 174.
 C₁₇H₁₀OCl₂. 1,4-Dichloro-8-acetoxy-5-methylantraquinone (WALSH and WEIZMANN), T., 690.
 C₁₇H₁₀ON. *O*-Benzoyl-2-cyano-1-hydrindone (MITCHELL and THORPE), T., 2273.
 C₁₇H₁₀ON₃. *o*, and *p*-Nitro-*o*-carboxybenzene-4-azo- α -naphthol (BALY, TUCK, and MARSDEN), T., 1601.
 C₁₇H₁₀ON₂. Benzoyl-1-aminonaphthyl-4-azoimide (MORGAN and COUZENS), T., 1697.
 C₁₇H₁₀ON₃. Benzoyl-1-aminonaphthalene-4-diazonium azide (MORGAN and COUZENS), T., 1697.
 C₁₇H₁₀O₂N₄. Azo derivative of 2,5-dinitro-1-methoxy-3:4-quinonediazide (MELDOLA and REVERDIN), T., 1206.
 Substance, from formo- α - and β -naphthalide and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.
 C₁₇H₁₀ON₂. Quinolineazophenyl acetate (FOX), T., 1346.
 C₁₇H₁₀ON. ω -Phthalimino-*o*-methoxyacetophenone (TUTIN), T., 2517.
 ω -Phthalimino-*p*-methoxyacetophenone (TUTIN), T., 2508.
 C₁₇H₁₀O₂N₂. 5-*p*-Acetylaminobenzeneazo-8-hydroxyquinoline, and its sodium salt (FOX), T., 1348.
 C₁₇H₁₀ON₂. Quinolineazophenetole (FOX), T., 1347.
 C₁₇H₁₀O₂N₂. 5-*p*-Ethoxybenzeneazo-8-hydroxyquinoline, and its sodium salt and hydrochloride (FOX), T., 1344.
 Ethoxyquinolineazophenol (FOX), T., 1347.
 C₁₇H₁₀ON₂. *p*-Dimethylaminoanilo- α -hydrindone (RUHEMANN), T., 1446.
 C₁₇H₁₀O₂N. Pukateine, and its salts (ASTON), T., 1382; P., 11.
 C₁₇H₁₀ON. Benzoyl derivative of β -3-methoxy-4:5-methylenedioxy-phenyl-methylamine (SALWAY), T., 1212.
 C₁₇H₁₀ON₂. 1-Methoxysuccindianilide (PURDIE and NEAVE), T., 1520.
 C₁₇H₁₀ON. 2-, 3-, and 4-Nitrobenzylidenecamphor (WOOTTON), T., 411, 412.
 C₁₇H₁₀ON₂. Benzylidenecamphorquinonehydrazone (FORSTER and ZIMMERLI), T., 2170.
 C₁₇H₁₀ON₂. $\alpha\beta$ -Dibenzylaminopropionic acid, and its dihydrochloride (FRANKLAND), T., 1688; P., 202.
 Phenylhydrazone of 4:5-dimethoxy-*o*-methylacetophenone (HARDING and WEIZMANN), T., 1128; P., 130.
 α -Benzoylcamphorquinonehydrazone (FORSTER and ZIMMERLI), T., 2169.
 C₁₇H₁₀ON. *d*-Camphorbenzylimide, preparation of (EVANS), T., 2240.
 Camphor *o*-, *m*-, and *p*-tolylimide (WOOTTON), T., 415.

- $C_{17}H_{20}O_2N_2$ Camphorquinone- α - and β -phenylcarbamyldiazotone (FORSTER and ZIMMERLI), T., 2174; P., 245.
 $C_{17}H_{23}O_2N$ Phenylurethane of Δ^3 -*m*-menthenol (8) (LUFF and PERKIN), T., 2153.
 Phenylurethane of Δ^3 -*p*-menthenol (8) (PERKIN and WALLACH), T., 1493.
 $C_{17}H_{23}O_3N$ *o*-, *m*-, and *p*-Tolyl- α -camphoramic acid (WOOTTON), T., 415.
 Hyoscyamine, specific rotatory power of (CARR and REYNOLDS), T., 1833; P., 180.

17 IV

- $C_{17}H_{11}ONS$ β -Aminonaphthathioxanthone, and its platinumchloride (DAVIS and SMILES), T., 1299; P., 174.
 $C_{17}H_{14}O_4N_2S_2$ Substance, from immidialipdone (FRANK), T., 2045; P., 218.
 $C_{17}H_{19}O_2N_2S$ Methanesulphonyl-*p*-aminobenzenediazo- β -naphthol (MORGAN, PICKARD, and MICKLETHWAIT), T., 63.
 $C_{17}H_{15}O_3NCl$ Phenylurethanes of γ -chloro- β -hydroxy- α -, and *p*-tolyl-, propane (BOYD and MARLE), T., 1790; P., 209.

 C_{18} Group.

- $C_{18}H_{13}N_2$ *oo*-Dicyano-*ss*'-diphenylisobutyronitrile (MITCHELL and THORPE), T., 2280.
 $C_{18}H_{14}O_5$ Acetyl derivative of pratol (POWER and SALWAY), T., 233.
 $C_{18}H_{16}O_4$ *p*-Carbethoxydihenzoylmethane (SMEDLEY), T., 1491.
 $C_{18}H_{16}O_5$ *oo*-Dicarboxy-*ss*'-diphenylisobutyric acid (MITCHELL and THORPE), T., 2281.
 $C_{18}H_{18}O_5$ Diacetyl derivative of 2:4-dihydroxy-4'-methoxybenzhydro (POPE and HOWARD), T., 973.
 $C_{18}H_{20}O_3$ Menthyl phenylacetate (COHEN and DUDLEY), T., 1749.
 Menthyl *o*-, *m*-, and *p*-toluate (COHEN and DUDLEY), T., 1749.
 $C_{18}H_{20}O_3$ Menthyl *o*-, *m*-, and *p*-methoxybenzoate (COHEN and DUDLEY), T., 1739.

18 III

- $C_{18}H_{15}O_2N_2$ 2-*o*-Carboxybenzoylindonoglyoxaline, and its silver salt (RUEHMANN), T., 1442.
 $C_{18}H_{19}ON_4$ Quinolinediazo-8-hydroxyquinoline, and its sodium salt and hydrochlorides (FOX), T., 1345.
 $C_{18}H_{17}O_2N_4$ Substance, from carbazole and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.
 $C_{18}H_{15}NS$ *N*-Phenylthiodiphenylamine (BARNETT and SMILES), T., 364.
 $C_{18}H_{17}O_2N$ ω -Phthalimino-*op*-dimethoxyacetophenone (TUTIN), T., 2513.
 $C_{18}H_{19}O_2N_7$ Substance, from 2:4-diaminoazobenzene and trinitrobenzene (SUDBOROUGH and BEARD), T., 787.
 $C_{18}H_{19}O_3N_2$ *pp'*-Dimethoxy-2:5-diphenylpyrazine, and its salts (TUTIN), T., 2505; P., 244; (TUTIN and CATON), T., 2531; P., 245.
pp'-Dimethoxy-2:6-diphenylpyrazine, and its salts (TUTIN), T., 2506; P., 244; (TUTIN and CATON), T., 2532; P., 245.
 $C_{18}H_{19}O_2N_4$ Substance, from α -amino- β -naphthyl ethyl ether and trinitrobenzene (SUDBOROUGH and BEARD), T., 787.
 $C_{18}H_{19}O_3N_4$ Substance, from ethyl 2-aminoindene-3-carboxylate and trinitrobenzene (SUDBOROUGH and BEARD), T., 788.
 $C_{18}H_{19}O_3N$ 8-Methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline, and its hydrochloride (+2H₂O) and picrate (SALWAY), T., 1214.
 6-Methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline, and its hydrochloride and picrate (SALWAY), T., 1215.

- C_8H_5ON Phenylhydrazone of ethyl 1-hydrindone-2-carboxylate (MITCHELL and THORPE), T., 2273.
- $C_8H_5O_2N_2$ *cis*-Tetrahydrofuran-2,5-dicarboxyldianilide (LE SUEUR and HAAS), T., 184.
- $C_8H_5O_2N_2$ Acid diamide of ω -dicarboxy- $\beta\beta'$ -diphenylisobutyric acid (MITCHELL and THORPE), T., 2281.
- $C_8H_5O_2N_2$ Substance, from ethyl β -anilinoacrylate and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.
- $C_8H_5N_3Sb$ Tri-*p*-aminotriphenylstibine (MAY), P., 142.
- C_8H_5ON β -Benzyl- γ -benzylaminomethylhydantoin, and its hydrochloride (FRANKLAND), T., 1689; P., 203.
- Benzoyl derivative of camphane-oxytriazine (FORSTER and ZIMMERLI), T., 2177.
- C_8H_5ON Phenylacetyl- β -3-methoxy-4:5-methylenedioxyphenylethylamine (SALWAY), T., 1213.
- $C_8H_5O_2N_2$ Dimethoxydiphenacylamine, hydrochloride of (TUTIN), T., 2507.
- $C_8H_5O_2N_2$ Diacetyl-3-ethoxybenzidine (CAIN and MAY), T., 725.
- $C_8H_5O_2N_2$ Phenylhydrazone of hydroxydiacetyldimethoxybenzene (TUTIN and CATON), T., 2066.
- $C_8H_5O_2N_2$ β -Benzylamino- α -benzylcarbamidopropionic acid (FRANKLAND), T., 1689; P., 203.
- C_8H_5ON Hydroxycodine, and its salts (DOBNIK and LAUDER), P., 339.
- $C_8H_5O_2N_2$ Acetyl derivative of 3-amino-phenyl- α -camphoric acid (WOOTTON), T., 414.
- C_8H_5ON 4-Ethoxyphenyl- α -camphoric acid (WOOTTON), T., 415.

18 IV

- $C_8H_5O_2N_3Sb$ Trinitrotriphenylstibine (MAY), P., 142.
- $C_8H_5O_2N_2Br$ Acetyl derivative of substance, from α -bromo- β -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.
- $C_8H_5O_2N_3Sb$ Trinitrotriphenylstibine dihydroxide, and its dichloride (MAY), T., 1958.
- $C_8H_5O_2SSb$ Triphenylstibine sulphate (MAY), T., 1958.
- C_8H_5OCISb Triphenylstibine hydroxychloride (MORGAN, MICKLETHWAIT, and WHITEY), T., 37.
- $C_8H_5O_2NSb$ Triphenylstibine hydroxynitrate (MORGAN, MICKLETHWAIT and WHITEY), T., 35.

C_{19} Group.

- $C_{19}H_{12}O$ 3-Hydroxy-9-phenylfluorone (POPE and HOWARD), T., 1026.
- $C_{19}H_{12}O_2$ 3,6-Dihydroxy-9-phenylxanthen (POPE and HOWARD), T., 81.
- $C_{19}H_{12}O_2$ Piperonylidene-4:5-dimethoxy- α -methylacetophenone (HARDING and WEIZMANN), T., 1128.
- $C_{19}H_{12}O_2$ Matairesinol (+ Et OH) (EASTERFIELD and BEE), T., 1025; P., 7.
- $C_{19}H_{12}O_2$ Benzoyloxydiacetyldimethoxybenzene (TUTIN and CATON), T., 2066.
- $C_{19}H_{12}O_2$ Matairesinolic acid (+ $3H_2O$), and its calcium salt (EASTERFIELD and BEE), T., 1031; P., 7.
- $C_{19}H_{12}Si$ Dibenzylethylpropylsilicane (CHALLENGER and KIPPING), T., 146; P., 3.
- $C_{19}H_{12}O_2$ Menthyl *o*-, *m*-, and *p*-ethoxybenzoate (COHEN and DUDLEY), T., 1741.
- $C_{19}H_{12}N_2$ Menthylethylbenzamidine, and its salts (COHEN and MARSHALL), T., 333.

$C_{15}H_{20}O_{11}$ Methyl pentamethylgynocardinate (MOORE and TUTIN), T. 1287; P., 182.

$C_{15}H_{25}N$ Tridecylaniline, and its hydrochloride (LE SUEUR, T., 2440; P., 492).

$C_{15}H_{21}O_4$ Diisoamyl α -thujadicarboxylate (THOMSON), T., 1514; P., 175.

19 III

$C_{15}H_{10}O_2Br_4$ Tetrabromo-3-hydroxy-9-phenylfluorone (POPE and HOWARD, T., 82).

$C_{15}H_{13}O_5N_4$ Substance, from acridine and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.

Substance, from α - and β -naphthoquinoline and trinitrobenzene (SUDBOROUGH and BEARD), T., 795.

$C_{15}H_{13}ON_3$ 5- α -Naphthaleneazo-8-hydroxyquinoline, and its hydrochloride and sodium salt (FOX), T., 1345.

Quinoline-3-azo- β -naphthol (MILLS and WATSON), T., 753; P., 56.

$C_{15}H_{17}O_2N_2$ α - ω -Tricyano- $\beta\beta'$ -diphenylisobutyric acid, and its potassium salt (MITCHELL and THORPE), T., 2250.

$C_{15}H_{11}O_2N_6$ Substance, from *m*-nitrobenzaldehydephenylhydrazone and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.

$C_{15}H_{15}NS$ Diphenylthiobenzamide, preparation of (RUSSELL), T., 956.

$C_{15}H_{15}O_2N_3$ Benzoyl-4-nitroethyl- α -naphthylamine (MORGAN and COUZENS), T., 1693.

$C_{15}H_{11}O_2N_4$ Substance, from benzyaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 788.

$C_{15}H_{17}O_2N_3$ Nitrosamine, from hydrolysis of benzoyl-4-aminonaphthalene-1-diazonium salts (MORGAN and COUZENS), T., 1695.

$C_{15}H_{15}ON_2$ *as*-Benzoyl-ethyl-1:4-naphthalenediamine (MORGAN and COUZENS), T., 1693; P., 165.

$C_{15}H_{15}O_3N_2$ *cyclo*Pentau-1-one-2:5-dicarbanilide (MITCHELL and THORPE), T., 1003.

$C_{15}H_{15}O_3N_4$ 1:7-Dibenzyltetrahydrouric acid (FRANKLAND), T., 1691; P., 203.

$C_{15}H_{20}O_{12}S_2$ Matairesinoldisulphonic acid, barium salt (+5H₂O) (EASTFIELD and BEE), T., 1030; P., 7.

$C_{15}H_{21}O_2N$ Laureline, and its salts (ASTON), T., 1386; P., 11.

$C_{15}H_{22}O_2N_2$ Ethyl 3-anilino-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanacetate (CROSSLEY and GILLING), T., 527.

$C_{15}H_{23}O_2N$ Menthyl *o*- and *p*-dimethylaminobenzoate (COHEN and DULEY), T., 1746.

$C_{15}H_{22}ON_2$ Phenyltridecylnitrosoamine (LE SUEUR), T., 2440.

19 IV

$C_{16}H_{15}O_3N_3S$ Dinitro-*S*-salicylphenazothionium hydroxide (BARNET and SMILES), T., 372.

$C_{16}H_{15}ON_2Cl$ Benzoyl-ethyl-4-aminonaphthalene-1-diazonium chloride (MORGAN and COUZENS), T., 1695.

$C_{16}H_{15}O_2N_3Cl$ Benzoyl-ethyl-4-aminonaphthalene-1-diazonium perchlorate (MORGAN and COUZENS), T., 1695.

$C_{16}H_{17}O_2N_3S$ Benzoyl-ethyl-4-aminonaphthalene-1-diazonium sulphate (+ EtOH) (MORGAN and COUZENS), T., 1694.

$C_{16}H_{36}O_3SSi$ *N*-Dibenzylethylpropylsilicanesulphonic acid, metallic salt of (CHALLENGER and KIPPING), T., 152; alkaloidal salts of (CHALLENGER and KIPPING), T., 760.

N-Dibenzylethylpropylsilicanesulphonic acid, alkaloidal salts of (CHALLENGER and KIPPING), T., 760.

$\text{H}_2\text{O}, \text{S}, \text{Si}$ Dibenzylethylpropylsilicanedisulphonic acid, metallic salts of (CHALLENGER and KIPPING), T., 153.

19 V

$\text{H}, \text{ON}, \text{Cl}, \text{Sn}$ Benzylethyl-4-aminonaphthalene-1-diazonium perchloride (MORGAN and COUZENS), T., 1695.

C_{20} Group.

H_2O_2 9-Phenyl-2-methylfluorone (POPE and HOWARD), T., 1026.

H_2O_2 6-Hydroxy-9-phenyl-2-methylxanthen (POPE and HOWARD), T., 81.

H_2O_2 3,6-Dihydroxy-4'-methoxy-9-phenylxanthen (POPE and HOWARD), T., 974.

H_2O_2 1,2,8-Dihydroxy-2,3,8-triphenylethane (McKENZIE and WREN), T., 430.

H_2N 2-tert.-Butyl-4,5-diphenylpyrrole (BOON), T., 1280; P., 95.

H_2O Desylpinacolium (*α*-tert.-butyl-β-benzoylphenylethane) (BOON), T., 1258.

H_2O α- and β-Naphthyl hydrogen camphorate (EDMINSON and HILDITCH), T., 227.

H_2O 2,4,6-Trimethoxyphenyl 3,4-dimethoxystyryl ketone (TUTIN and CATON), T., 2067; P., 223.

H_2O o-8-Acetylrinylphenyl hydrogen camphorate (EDMINSON and HILDITCH), T., 227.

H_2N_2 Ethylidenexylidine, bimolecular (JONES and WHITE), T., 641; absorption spectrum of (PERVIS), T., 645.

H_2O Menthyl o-, and p-allyloxybenzoate (COHEN and DUDLEY), T., 1745.

H_2O Menthyl o-, m-, and p-propoxybenzoate (COHEN and DUDLEY), T., 1742.

Menthyl o- and p-isopropoxybenzoate (COHEN and DUDLEY), T., 1743.

H_2O Phytosterol, from colocynth (POWER and MOORE), T., 108.

20 III

$\text{H}_2\text{O}, \text{S}$ Dinaphthylene p-disulphoxide (HILDITCH), T., 2591.

H_2ON 6o-Phenylmethylacetylcyclopentenephazazine (RUEHMANN), T., 1444.

H_2ON Benzylethyl-4-aminonaphthalene-1-diazonium cyanide (MORGAN and COUZENS), T., 1695.

H_2ON Salicylphenylbenzamidine (TITHERLEY), T., 209; P., 9.

H_2ON Anhydrocotarninenitrophthalide (HOPE and ROBINSON), P., 230.

H_2ON 8-Hydroxy-5-phenyl-3-methyldihydroacridine (POPE and HOWARD), T., 83.

H_2ON Berberine, constitution of (PERKIN and ROBINSON), T., 305; P., 24.

H_2ON Substance, from ω-diaminostilbene and trinitrobenzene (SUDBOROUGH and BEARD), T., 791.

$\text{H}_2\text{O}, \text{S}$ Substance, from 2,3-diketo-1-acetyl-4-phenyl-5-methylcyclopentene and phenylmercaptan (RUEHMANN), T., 1444.

H_2ON Anhydrocotarnineaminophthalide (HOPE and ROBINSON), P., 230.

- $C_{20}H_{20}O_4N_2$ *mm'pp'*-Tetramethoxy-2:5-diphenylpyrazine, and its salts (TUTIN), T., 2510; P., 244; (TUTIN and CATON), T., 2533; P., 245.
mm'pp'-Tetramethoxy-2:6-diphenylpyrazine, and its salts (TUTIN, T. 2511; P., 244; (TUTIN and CATON), T., 2533; P., 245.
- $C_{20}H_{20}O_2N$ α -, and β -Naphthylcamphorimide (WOOTTON), T., 415.
- $C_{20}H_{20}O_2N$ Papaverine, constitution of the reduction products of (PYMAN and REYNOLDS), T., 1320; P., 180.
- $C_{20}H_{20}O_4S$ α - and β -Naphthyl camphor- β -sulphonate (EDMUNSON and HILDITCH), T., 228.
- $C_{20}H_{20}O_2N$ Oxime of desylpinacoline (BOON), T., 1258.
- $C_{20}H_{20}O_3N$ α - and β -Naphthyl α -camphoramic acid (WOOTTON), T., 415.
- $C_{20}H_{20}O_3N$ Pavine, and its hydriodide (PYMAN and REYNOLDS), T., 1327; P., 180; preparation and resolution of (POPE and GIBSON), T., 2207; P., 250.
 d - and l -Pavine, rotatory power of salts of, with d -tartaric acid and d - and l -camphor- β -sulphonic acid (POPE and GIBSON), T., 2211; P., 250.
- $C_{20}H_{20}O_2N_2$ Ethyl 3-methylanilino-1:1-dimethyl- Δ^2 -cyclohexenylidene- γ -cyanoacetate (CROSSLEY and GILLING), T., 527.
 Dioxime of desylpinacoline (BOON), T., 1259.
- $C_{20}H_{20}O_4S$ α - β -Acetylvinylphenyl camphor- β -sulphonate (EDMUNSON and HILDITCH), T., 228.
- $C_{20}H_{20}O_4S_2$ Dicapphoryl β - α -disulphoxide (HILDITCH), T., 1096; P., 95.
- $C_{20}H_{20}O_4P$ Dicapphorylphosphinic acid, and its metallic salts (MORGAN and MOORE), T., 1697.

20 IV

- $C_{20}H_{15}O_3NS$ Tetranitro- S -phenetylphenazothionium hydroxide, and sulphate (BARNETT and SMILES), T., 368.
- $C_{20}H_{15}O_2N_2Cl_2$ 4:4'-Dichlorobenzilphenylhydrazine (KENNER and WITMAN), T., 1967.
- $C_{20}H_{25}O_2BrS$ d -Bornylamine d - α -bromocamphor- π -sulphonate (POPE and READ), T., 994.

20 V

- $C_{20}H_{15}ONCl_4S$ Tetrachloro- S -phenetylphenazothionium hydroxide (+ H_2O , $CHCl_3$) (BRADY and SMILES), T., 1561.
- $C_{20}H_{25}ONBrS$ d -(l)-Tetrahydroquinaldine d -(l)- α -bromocamphor- π -sulphonate (POPE and READ), T., 2203.

C₂₁ Group.

- $C_{21}H_{15}O_4$ 3-Acetoxy-9-phenylfluorone (POPE and HOWARD), T., 1027.
- $C_{21}H_{15}O_6$ Ethyl 2-keto-3-acetoxy-4:5-diphenylene-2:3-dihydrofuran-2-carboxylate (RICHARDS), T., 1457; P., 195.
- $C_{21}H_{15}O_9$ Acetyl derivative of substance, from red clover flowers (POWER and SALWAY), T., 239.
- $C_{21}H_{17}N$ 2:3-Diphenyl-1-methylindole, preparation of (RICHARDS), T., 97.
- $C_{21}H_{18}O_3$ 6-Hydroxy-4'-methoxy-9-phenyl-2-methylxanthen (POPE and HOWARD), T., 974.
- $C_{21}H_{25}O_2$ 6- α -Methoxy- α -88-triphenylethane (MCKENZIE and WREN), T., 189.
 l - α -Methoxy- α -88-triphenylethane (MCKENZIE and WREN), T., 453.
- $C_{21}H_{25}O_{11}$ Quercitrin, and its trisodium derivative (MOORE), P., 182.
- $C_{21}H_{26}O_{12}$ Serotrin (+ $3H_2O$) (POWER and MOORE), T., 1109; P., 124.
 Incarnatin, from clover flowers (ROGERSON), T., 1008; P., 112.
- $C_{21}H_{22}O_7$ Acetylmatairesinol (EASTERFIELD and BEE), T., 1030; P., 7.
- $C_{21}H_{24}N_2$ Menthylidiethylbenzamidine, and its salts (COMES and MARSHALL), T., 333.

- $C_{27}H_{40}O$ Trifolialanol (POWER and SALWAY), T., 249; P., 20.
 $C_{27}H_{41}N$ Pentadecylaniline, and its hydrochloride (LE SUEUR), T., 2433; P., 240.

21 III

- $C_{21}H_{13}OCl$ 1 (or 4)-Chloro-8-hydroxy-4 (or 1)-phenoxy-5-methylantraquinone (WALSH and WEIZMANN), T., 690.
 $C_{21}H_{15}ON_2$ Diphenylhydrazone of triketohydrindene (RUEHMANN), T., 1445.
 $C_{21}H_{27}O_2N_2$ Ethyl α - β -tricyano- $\beta\beta'$ -diphenylisobutyrate (MITCHELL and THORPE), T., 2280.
 $C_{21}H_{27}O_2N$ 8-Hydroxy-5-*p*-methoxyphenyl-3-methyldihydroacridine (POPE and HOWARD), T., 975.
 $C_{21}H_{27}O_2N_2$ Strychnine, constitution of (PERKIN and ROBINSON), T., 305; P., 24.
 Substance, from piperidine and diketodiphenylpyrrolone (RUEHMANN), T., 465.
 $C_{21}H_{27}O_2N$ *N*-Methylpavine, and its salts (PYMAN and REYNOLDS), T., 1324; P., 189.
 $C_{21}H_{27}ON$ Laudanosine hydrogen oxalate (+1½ or 2½H₂O) (PYMAN and REYNOLDS), T., 1323.
 $C_{21}H_{27}ON$ Acetotridecylaniline (LE SUEUR), T., 2440.
 $C_{21}H_{27}ON_2$ Phenylpentadecylnitrosoamine (LE SUEUR), T., 2430.

21 IV

- $C_{22}H_{19}O_4NS$ Dinitro-*S*-mesitylphenazothionium hydroxide (+H₂O) (BARNETT and SMILES), T., 371.
 $C_{22}H_{19}O_4NS$ Phenetoleazosulphobenzylidene-*p*-nitroaniline, potassium salt (GREEN and SEN), T., 2245.
 $C_{22}H_{19}O_4NS$ Phenetoleazosulphobenzylideneaniline (GREEN and SEN), T., 2244.
 $C_{22}H_{19}O_4NS$ Phenetoleazosulphobenzylidene-*p*-aminophenol, potassium salt (GREEN and SEN), T., 2245.
 $C_{22}H_{19}O_5NS_2$ Phenetoleazosulphobenzylideneaniline-*p*-sulphonic acid, potassium salt (GREEN and SEN), T., 2244.
 $C_{22}H_{19}O_4N_2Cl$ 6(or 7)-Methoxy-7(or 6)-[6:7-dihydroxy-2-methyl-3:4-dihydroisoquinoliniumoxy]-2-methyl-3:4-dihydroisoquinolinium chloride (PYMAN), T., 278.
 $C_{22}H_{19}O_4NI$ 6(or 7)-Methoxy-7(or 6)-[6:7-dihydroxy-2-methyl-3:4-dihydroisoquinoliniumoxy]-2-methyl-3:4-dihydroisoquinolinium iodide (PYMAN), T., 279.

C₂₂ Group.

- $C_{22}H_{14}$ $\alpha\beta\beta'$ -Dinaphthanthracene, preparation of (HOMER), T., 1141; P., 12; absorption spectra of, and of its hydro-derivative and isomerides (HOMER and PURVIS), T., 1155; P., 25.

22 II

- $C_{22}H_{15}N_2$ Diphenylpyrrolinophenazine (RUEHMANN), T., 1443; P., 196.
 $C_{22}H_{15}O$ Phenylethylidenedeoxybenzoin (RUEHMANN), T., 459.
 $C_{22}H_{17}O_2$ Triphenylbutyrolactone (FURDE and ARUP), T., 1548; P., 199.
 $C_{22}H_{17}O_2$ Substance, from ethyl acetoacetate and phenanthraquinone (RICHARDS), T., 1480; P., 195.
 $C_{22}H_{17}N$ 2:3-Diphenyl-1-ethylindole (RICHARDS), T., 978.
 $C_{22}H_{17}O_3$ Ethyl 9-phenanthroxylacetoxyacetoacetate (RICHARDS), T., 1480; P., 195.

- $C_{22}H_{20}O_{11}$ Trifolin (+H₂O) (POWER and SALWAY, T., 239; P., 20.
 139) Trifolin (POWER and SALWAY, T., 244; P., 20.
 $C_{22}H_{20}O_2$ Diphenylcampholide (SHIBATA, T., 1240.
 Lactone of diphenylhydroxycampholic acid (SHIBATA, T., 1241.
 $C_{22}H_{24}O_3$ 2-Aceto- α -naphthyl hydrogen camphorate (EDMINSON and HIL-
 DITCH), T., 228.
 $C_{22}H_{20}O_3$ Diphenylhydroxycampholic acid, barium salt of (SHIBATA, T.,
 1240.
 Diphenylhydroxyisocampholic acid (SHIBATA, T., 1245.
 $C_{22}H_{20}O_3$ Menthyl α - and β -methoxynaphthoate (COHEN and DUDLEY,
 T., 1747.
 $C_{22}H_{24}O_3$ Menthyl o -, m -, and p -isomethoxybenzoate (COHEN and
 DUDLEY, T., 1744.
 $C_{22}H_{28}O_4$ Citrullol, from colocynth (POWER and MOORE), T., 102; P., 3.

22 III

- $C_{22}H_{14}O_{10}N_8$ 4:4':7:7'-Tetranitro-6:6'-dihydroxy-1:1'- p -phenylene-2:2'-di-
 methylbisbenziminazole (MELDOLA and KUNTZEN), P., 340.
 $C_{22}H_{10}O_4N$ Substance, from ω -amino- op -dihydroxyacetophenone (TUTIN), T., 2315.
 $C_{22}H_{16}O_6N_4$ Substance, from trinitrobenzene and phenyl- β -naphthylamine (SIL-
 BOROUGH and BEARD), T., 789.
 $C_{22}H_{16}O_6N_4$ Substance, from 1-benzeneazo-2-naphthylamine and trinitrobenzene
 (SILBOROUGH and BEARD), T., 787.
 $C_{22}H_{22}O_8N_2$ Dinitrodiphenylcampholide (SHIBATA, T., 1241.
 $C_{22}H_{22}O_8N$ Nitrognoscopine, and its salts (HOPE and ROBINSON), P., 229.
 $C_{22}H_{22}O_7N$ Gnoscopine (*di-narcotine*), synthesis of (PERKIN and ROBINSON),
 P., 46; resolution of (PERKIN and ROBINSON), P., 131.
d- and *l*-Narcotine, *d*-bromocamphorsulphonates of (PERKIN and ROBINSON),
 P., 131.
 $C_{22}H_{21}O_8S$ 2-Aceto- α -naphthyl camphor- β -sulphonate (EDMINSON and
 HILDITCH), T., 228.
 $C_{22}H_{24}O_4N$ Aminognoscopine (HOPE and ROBINSON), P., 230.
 $C_{20}H_{20}O_6N_2$ $\alpha\beta$ -Dianilinoheptic acid, and its silver salt (LE SUEUR and
 HAAS), T., 180.

22 IV

- $C_{22}H_{17}O_2NS$ Substance, from phenylmercaptan and diketodiphenylpyrrole
 (RUHEMANN), T., 464.
 $C_{22}H_{19}O_2N_2S$ Phenetoleazosulphobenzylideneaminosalicylic acid,
 potassium salt (GREEN and SEN), T., 2245.
 $C_{22}H_{24}O_2N_2S$ Phenetoleazosulphobenzylidene- p -phenylenedimethylid-
 amine, potassium salt (GREEN and SEN), T., 2245.
 $C_{22}H_{27}O_2N_2Cl$ 6 (or 7)-Methoxy-7 (or 6)-[7 (or 6)-hydroxy-6 (or 7)-methoxy-
 2-methyl-3:4-dihydroquinolinium oxy]-2-methyl-3:4-dihydro-
 quinolinium chloride (PYMAN), T., 278.

 C_{23} Group.

- $C_{23}H_{16}O_2$ 4:5:6-Triphenyl-2-pyrone (RUHEMANN), T., 459; P., 59.
 8-Hydroxy-11-phenyl- β -naphthaxanthene (POPE and HOWARD), T., 92.
 $C_{23}H_{17}N_8$ Phenyl- p -tolylpyrrolinophenazine (RUHEMANN), T., 1444.
 $C_{23}H_{18}O_8$ Triacetylprateusol (POWER and SALWAY), T., 238.
 $C_{23}H_{20}O_4$ 6-Acetoxy-4'-methoxy- p -phenyl-2-methylxanthene (POPE and
 HOWARD), T., 974.

- 2. H_2O Ethyl phenanthroxylacetoxymalonate (RICHARDS), T., 1457;
P., 195.
- 2. H_2O Methyl diphenylhydroxyisocampholate (SHIRATA), T., 1245.
- 2. H_2N Phenylmethylbenzamidine, and its hydrochloride and platinum
salt (COHEN and MARSHALL), T., 330.
- 2. H_2N Heptadecylaniline, and its hydrochloride (LE SUEUR), T., 2435;
P., 290.

23 III

- 2. $\text{H}_2\text{O.N}_2$ Substance, from benzyldene- α -naphthylamine and trinitrobenzene
SUDBOROUGH and BEARD), T., 793.
- 2. Substance, from α -diphenylpyridine and trinitrobenzene (SUDBOROUGH and
BEARD), T., 794.
- 2. H_2ON 10-Hydroxy-7-phenyldihydro- $\alpha\beta$ -phenonaphthacridine (POPE
and HOWARD), T., 976.
- 2. $\text{H}_2\text{O.Cl}$ 3:6-Diacetoxy-9-phenylxanthonium chloride (POPE and
HOWARD), T., 1027.
- 2. $\text{H}_2\text{O.N}_2$ 3-Benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline,
decomposition of (RUHEMANN), T., 463.
- 2. $\text{H}_2\text{O.N}_2$ Substance, from α - and β -naphthylamine and trinitrobenzene
SUDBOROUGH and BEARD), T., 788.
- 2. $\text{H}_2\text{O.N}$ Dibenzoyl derivative of μ -hydroxyphenylethylmethylamine
(WALPOLE), T., 946.
- 2. Acetoxy-5- μ -methoxyphenyl-3-methylidihydroacridine (POPE and
HOWARD), T., 975.
- 2. $\text{H}_2\text{O.N}_2$ Substance, from tetramethyldiaminobenzophenone and trinitro-
benzene (SUDBOROUGH and BEARD), T., 792.
- 2. $\text{H}_2\text{O.N}_2$ Substance, from tetramethyl- μ -diaminodiphenylmethane and tri-
nitrobenzene (SUDBOROUGH and BEARD), T., 791.
- 2. $\text{H}_2\text{O.N}_2$ Substance, from tetramethyldiaminobenzhydrol and trinitrobenzene
(SUDBOROUGH and BEARD), T., 792.
- 2. $\text{H}_2\text{O.N}_2$ Nitronarecine (HOPE and ROBINSON), P., 230.
- 2. $\text{H}_2\text{O.N}$ Acetopentadecylanilide (LE SUEUR), T., 2439.
- 2. $\text{H}_2\text{O.N}_2$ Phenylheptadecylnitrosoamine (LE SUEUR), T., 2137.

23 IV

- 2. $\text{H}_2\text{O.N.S}$ Toluene- α -sulphonyl- p -aminobenzeneazo- β -naphthol (MOR-
GAN and PICKARD), T., 57.
- 2. $\text{H}_2\text{O.N.S}$ Substance, from tetramethyldiaminothiobenzophenone and trinitro-
benzene (SUDBOROUGH and BEARD), T., 792.

C_{24} Group.

- 2. H_2O Benzoyl derivative of 2-benzo- α -naphthol (EDMONSON and HIL-
LARY), T., 226.
- 2. H_2O 8-Hydroxy-11- μ -methoxyphenyl- β -naphthaxanthen (POPE and
HOWARD), T., 975.
- 2. H_2O Acetyl derivative of trifolitin (POWER and SALWAY), T., 210.
- 2. H_2O Acetyl derivative of substance, from red clover flowers (POWER and
SALWAY), T., 238.
- 2. H_2O 3:6-Diacetoxy-4'-methoxy-9-phenylxanthen (POPE and HOWARD),
T., 974.
- 2. H_2O Tetra-acetylhesperitin (TUTIN), T., 2061.
- 2. H_2O Menthyl o -, and p -benzyloxybenzoate (COHEN and DUDLEY), T.,
1717.

- $C_{24}H_{10}O_5$ Elaterone (MOORE), T., 1803; P., 215.
 $C_{24}H_{20}O_4$ Substance, from oxidation of elateric acid (MOORE), T., 1804; P., 215.
 $C_{24}H_{28}N_2$ *o*-, *m*-, and *p*-Tolylmenthylbenzamidines, and their hydrochlorides, and platinichlorides (COHEN and MARSHALL), T., 331.
 $C_{24}H_{40}O_2$ Starch, iodine reaction for (HARRISON), P., 252.

24 III

- $C_{24}H_{18}O_2S_2$ Naphthabisthioxanthone (DAVIS and SMILES), T., 1268; P., 114.
 $C_{24}H_{18}O_2N_4$ Acetyl derivative of substance, from phenyl- β -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 789.
 $C_{24}H_{19}O_3N$ 10-Hydroxy-7-*p*-methoxyphenyldihydro- $\alpha\beta$ -phenonaphthacridine (POPE and HOWARD), T., 976; P., 88.
 $C_{24}H_{23}O_2N_4$ Substance, from benzyl- β -naphthylamine and trinitrotoluene (SUDBOROUGH and BEARD), T., 788.
 $C_{24}H_{25}O_6N_6$ Substance, from diethylaminobenzylidene-*p*-aminomethylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 791.
 $C_{24}H_{26}O_2N$ Acetylaminogossypine (HOPKINS and ROBINSON), P., 230.
 $C_{24}H_{28}O_4N_2$ Methyl $\alpha\beta$ -dianilinosuccinate (LE SUEUR and HAAS), T., 194.
 $C_{24}H_{32}O_3N_2$ Dioxime of elaterone (MOORE), T., 1804.

24 IV

- $C_{24}H_{18}O_2N_4S_3$ Benzene-1:3:5-trisulphonylter-*p*-phenylenediazoimide (MORGAN and PICKARD), T., 54.
 $C_{24}H_{18}O_2N_4S_3$ Benzene-1:3:5-trisulphonylter-*m*- and *p*-nitrosulfoxide (MORGAN and PICKARD), T., 54.
 $C_{24}H_{18}N_4Cl_4Pt$ Benzeneazobenzenediazonium platinichloride (HEWITT and THOLE), T., 515; P., 54.
 $C_{24}H_{24}O_2N_4S_3$ Benzene-1:3:5-trisulphonylter-*p*-phenylenediamine (MORGAN and PICKARD), T., 55.

C₂₅ Group.

- $C_{25}H_{34}O_{12}$ Carthamine, and its potassium salt (KAMETAKA and PERKIN), T., 1415; P., 181.
 Xanthocarthaninic acid, salts of (KAMETAKA and PERKIN), T., 1423; P., 181.
 $C_{25}H_{28}O_5$ *o*- β -Benzoylvinylphenyl hydrogen camphorate (EDMUNDS and HILDITCH), T., 227.
 $C_{25}H_{28}N_2$ Phenylmenthylethylbenzamidines, and its salts (COHEN and MARSHALL), T., 331.
 $C_{25}H_{40}O_6$ Acetyl derivative of trifolialol (POWER and SALWAY), T., 243.

25 III

- $C_{25}H_{18}O_{12}N_2$ Substance, from benzylideneaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.
 $C_{25}H_{18}O_{12}N_4$ Substance, from benzaldehydephenylhydrazones and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.
 $C_{25}H_{20}O_2N$ Acetyl derivative of 10-hydroxy-7-phenyldihydro- $\alpha\beta$ -phenonaphthacridine (POPE and HOWARD), T., 977.
 $C_{25}H_{28}O_2N_4$ Hydrate of 2,3-bis-(*p*-dimethylaminoanilo)- α -hydrazinone (RUHEMANN), T., 1445; P., 196.
 $C_{25}H_{28}O_5S$ *o*- β -Benzoylvinylphenyl camphor- β -sulphonate (EDMUNDS and HILDITCH), T., 228.
 $C_{25}H_{28}O_2N_4$ Substance, from the action of *p*-triazobenzaldehyde on camphor- ψ -semicarbazide (FORSTER and JUDN), T., 261.
 $C_{25}H_{45}ON$ Acetoheptadecylanilide (LE SUEUR), T., 2437.

25 IV

- H.O.NS Phenetoleazosulphobenzylidene- α - and β -naphthylamine, salts (GREEN and SEN), T., 2246.
 H.O.NS Benzoyloscine *d*-camphorsulphonate (TUTIN), T., 1795; P., 215.

25 V

- H.O.NBrS Benzoyl-*d*-oscine *d*-bromocamphorsulphonate (TUTIN), T., 1795; P., 215.

C₂₆ Group.

- H.O. 1:4-Diphenoxyanthraquinone (WALSH and WEIZMANN), T., 688.
 H.O. α - γ -Diphenyl-1-naphthylallene- α -carboxylic acid (LAPWORTH and WECHSLER), T., 45.
 Substance, from diphenyl-naphthylallene-carboxylic acid and acetic acid (LAPWORTH and WECHSLER), T., 47.
 H.N 1:2:3-Triphenylindole (RICHARDS), T., 978.
 H.O. α - γ -Diphenyl-1-naphthylbutyrolactone (LAPWORTH and WECHSLER), T., 42.
 H.O. 8-Acetoxy-11-*p*-methoxyphenyl- β -naphthaxanthen (POPE and HOWARD), T., 975.
 H.N 1:4:5-Triphenyl-2-*tert*-butylpyrrole (BOON), T., 1260.
 H.N. 1-Anilino-2-*tert*-butyl-4:5-diphenylpyrrole (BOON), T., 1259; P., 94.
 1:3:4-Triphenyl-6-*tert*-butyldihydropyridazine (BOON), T., 1259; P., 94.
 H.O. Diacetyltrullol (POWER and MOORE), T., 102.

26 III

- H.O.N_2 Dinitro-1:4-diphenoxyanthraquinone (WALSH and WEIZMANN), T., 689.
 H.O.Br Bromolactone from ethyl α -diphenyl- γ -1-naphthylallene- α -carboxylate (LAPWORTH and WECHSLER), T., 47.
 H.O.N. Substance, from acetophenonephenylhydrazine and trinitrobenzene (SUDBOROUGH and BEARD), T., 794.
 H.O.N 10-Acetoxy-7-*p*-methoxyphenyldihydro- $\alpha\beta$ -phenonaphthacridine (POPE and HOWARD), T., 976.
 H.O.N_{10} Substance, from *p*-aminobenzeneazodimethylamine (SUDBOROUGH and BEARD), T., 787.
 H.O.N_2 Ethyl $\alpha\beta$ -dianilinosebacaate (LE SUEUR and HAAS), T., 150.

C₂₇ Group.

- H.O. 2:4-Dibenzoyloxybenzhydrol (POPE and HOWARD), T., 80.
 H.O. Tetraphenylacetone (SMEDLEY), T., 1491; P., 149.
 H.O. 2-Benzoyl- α -naphthyl hydrogen camphorate (EDMINSON and HUNTCH), T., 228.
 H.O. Rutin ($+3\text{H}_2\text{O}$), occurrence of, in *Tephrosia purpurea* (CLARKE and BANFEE), T., 1837; P., 213.
 Osyritrin (*violaquercitrin*), occurrence of, in *Osyris abyssinica* (AULD), P., 146.
 Osyritrin, myrticlorin, violaquercitrin and rutin ($+3\text{H}_2\text{O}$), identity of (PERKIN), T., 1776; P., 213.
 H.N. β -Bornyl ornylbenzamidine, and its salts (COHEN and MARSHALL), T., 324.

- $C_{27}H_{46}O$ Verosterol (+ H_2O) (POWER and ROGERSON), T., 1951; P., 215.
 Phytosterol, from colocynth (POWER and MOORE), T., 105.
 Phytosterol, from gelsemium (MOORE), T., 2226; P., 247.
 Phytosterol, (and + H_2O) from *Trifolium incarnatum* (ROGERSON), T., 1952; P., 112.

27 III

- $C_{27}H_{30}O_{12}N_8$ Substance, from cinnamaldehydephenylhydrazone and triethylbenzene (SUDBOROUGH and BEARD), T., 793.
 $C_{27}H_{31}O_2N$ 8-Benzoyloxy-5-phenyl-3-methyldihydroacridine (POPE and HOWARD), T., 83.
 $C_{27}H_{31}O_2N_3$ Quinine 4-oximinocyclohexanecarboxylate (+ $2\frac{1}{2}H_2O$) (MILLER and BAIN), T., 1872.

27 IV

- $C_{27}H_{20}O_2N_2S$ Phenetoleazosulphobenzylideneaminoazobenzene, potassium salt (GREEN and SEN), T., 2246.

 C_{28} Group.

- $C_{28}H_{20}O$ 2:2:5:5-Tetraphenyl-2:5-dihydrofuran (PURDIE and ARUP), T., 1542; P., 199.
 $C_{28}H_{22}O_2$ Ethyl α -diphenyl- γ -1-naphthylallene- α -carboxylate (LAWFORTH and WECHSLER), T., 44.
 $C_{28}H_{26}O_6$ Dibenzoyl derivative of 2:4-dihydroxy-4'-methoxybenzhydrol (POPE and HOWARD), T., 973.
 $C_{28}H_{26}O_3$ Menthyl β -benzoyloxynaphthoate (COHEN and DUDLEY), T., 114.
 $C_{28}H_{28}O_7$ α -Elaterin, constitution of (MOORE), T., 1797; P., 215.

28 III

- $C_{28}H_{19}O_{12}N_7$ Substance, from phenyl α - and β -naphthylamines and trinitrobenzene (SUDBOROUGH and BEARD), T., 789.
 $C_{28}H_{21}O_3N$ 2-Keto-3:3-bis(hydroxyphenyl)-4:5-diphenylpyrroline RUMMANN), T., 465.
 $C_{28}H_{22}O_2S$ Dibenzoyl-*p*-cresol sulphoxide (GAZDAR and SMILES), T., 2242.

 C_{29} Group.

- $C_{29}H_{44}N_2$ *d*-Bornyl-*l*-bornylethylbenzamidine, and its salts (COHEN and MARSHALL), T., 335.

29 III

- $C_{29}H_{19}O_{12}N_7$ Substance, from benzylidene- β -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.
 $C_{29}H_{21}ON$ α -Benzoylamino-*o*-dibenzoyloxyacetophenone (TINSLEY), T., 2515.
 $C_{29}H_{21}O_2N_7$ Substance, from *p*-tolyl- α -naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.
 Substance, from *o*- and *p*-tolyl- β -naphthylamines and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.
 $C_{29}H_{22}O_{12}N_8$ Substance, from tetramethyldiaminobenzophenone and trinitrobenzene (SUDBOROUGH and BEARD), T., 792.
 $C_{29}H_{22}O_2N_5$ Substance, from tetramethyldiaminotriphenylmethane and trinitrobenzene (SUDBOROUGH and BEARD), T., 792.

29 V

- C_8H_9ONSSi β -Naphthylamine *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 770.
 C_8H_9ONSSi γ -Menthylamine *dl*-dibenzylethylpropylsilicanesulphonate (+ $2H_2O$) (CHALLENGER and KIPPING), T., 152.

C₃₀ Group.

- $C_{30}H_{20}O_2$ 8-Benzoyloxy-11-phenyl- β -naphthaxanthen (POPE and HOWARD), T., 83.
 $C_{30}H_{20}N$ 1:2:3 Triphenyl- α and β -naphthindoles (RICHARDS), T., 979.
 $C_{30}H_{20}O_2$ 3:4-Dimethoxy-2:2:5:5-tetraphenyltetrahydrofuran (PURDIE and YOUNG), T., 1535; P., 198.

30 III

- $C_{30}H_{20}N_2$ *oo*-Dibenzoyloxy-2:5-diphenylpyrazine (TUTIN), T., 2519.
 $C_{30}H_{20}N_2$ Substance, from phenyl- α -naphthylamine and trinitrotoluene (STUBBING and BEARD), T., 789.
 $C_{30}H_{20}N_2$ Substance, from dibenzyl- β -naphthylamine and trinitrobenzene (STUBBING and BEARD), T., 791.
 $C_{30}H_{20}N_2$ Narcotine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 452.
 $C_{30}H_{20}N_2$ Elateronephenylhydrazone (MOORE), T., 1803.

30 IV

- $C_{30}H_{20}N_2S_2$ Bisphenetoleazobenzaldazinedisulphonic acid, potassium salt (GREEN and SEN), T., 2247.
 $C_{30}H_{20}NS$ *d*- and *l*-Pavine camphor- β -sulphonate (POPE and GIBSON), T., 2211.
 $C_{30}H_{20}NS$ *l*-Pavine camphor- β -sulphonate and *l*-pavine *d*-camphor- β -sulphonate (POPE and GIBSON), T., 2212.
 $C_{30}H_{20}Cl_3Sb$ Tricamphorylstibine chloride (MORGAN, MICKLETHWAIT, and WHITEY), T., 35.

30 V

- $C_{30}H_{20}NBrs$ *d*-Pavine *l*- α -bromocamphor- π -sulphonate (POPE and GIBSON), T., 2209.

C₃₁ Group.

- $C_{31}H_{20}O$ Prunol (+ H_2O), and its sodium salt (POWER and MOORE), T., 1104; P., 124.

31 III

- $C_{31}H_{20}N_2$ Substance, from dibenzyl- β -naphthylamine and trinitrotoluene (STUBBING and BEARD), T., 791.
 $C_{31}H_{20}N_2$ Aniline xanthocarthamate (KAMETAKA and PERKIN), T., 1424; P., 182.
 $C_{31}H_{20}N_2$ Brucine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 451.

31 IV

- $C_{31}H_{20}NS$ Strychnine *d*- and *l*-camphor- π -sulphonate (+ H_2O) (POPE and READ), T., 990.

C₃₂ Group.

C₃₂H₃₂O₃ Methylprunol (+ H₂O) (POWER and MOORE), T., 1106.

32 III

C₃₂H₂₈O₁₂N₂ Substance, from $\alpha\alpha$ - and $\beta\beta$ -dinaphthylamine and trinitrochlorobenzene (SUBBOROUGH and BEARD), T., 789.

C₃₃ Group.

C₃₃H₃₂O₅ 3:6-Dibenzoyloxy-9-phenylxanthen (POPE and HOWARD), T., 52.

C₃₃H₂₆O₈ Dibenzoylmatairesinol (EASIFFIELD and BEE), T., 1030.

C₃₃H₃₂O₈ Acetylprunol (POWER and MOORE), T., 1105.

33 III

C₃₅H₃₆O₇N₂ Brucine salt of β -phenyl- β -methylglycidic acid (WOOTTON), T., 409; P., 44.

33 IV

C₃₅H₂₆O₆N₂S₂ Methanedisulphonylbis-*p*-aminobenzeneazo- β -naphthol (MORGAN, PICKARD, and MICKLETHWAIT), T., 60.

C₃₄ Group.

C₃₄H₃₄O₄ Acetylmethylprunol (POWER and MOORE), T., 1106.

C₃₄H₇₆O Incarnatyl alcohol (ROGERS), T., 1011; P., 112.

34 III

C₃₄H₃₂O₄N₂ Substance, from *p*-nitrobenzaldehyde and sodium camphor (WOOTTON), T., 411.

C₃₅ Group.

C₃₅H₃₄O₅ Diacetylprunol (POWER and MOORE), T., 1105; P., 124.

35 III

C₃₅H₃₂O₁₂N β -Naphthylamine xanthocarthaminic acid (KANETAKA and PERKIN), T., 1425; P., 182.

C₃₅H₄₁O₆N₃ Ergotoxine, and its salts (BARGER and EWING), T., 284; P., 2.

C₃₆ Group.

C₃₆H₃₂O₆SSb₂ Triphenylstibine hydroxysulphate (MORGAN, MICKLETHWAIT, and WHITEY), T., 35.

C₃₆H₂₆O₆N₂S₂ Bisphenetoleazosulphobenzylidene-*p*-phenylenediamine potassium salt (GREEN and SEN), T., 2247.

C₃₆H₄₇O₆N₂Cl₃ Trichlorobutylidenebis-3-aminophenyl- α -camphoraminic acid (WOOTTON), T., 410.

36 V

C₃₇H₅₀O₅NSSi Morphine *dl*- and *ld*-dibenzylethylpropylsilicane-silicophosphate (CHALLENGER and KIPPING), T., 762.

C₃₇ Group.

C₃₇H₃₀O₂₀ Octa-acetylserotrin (POWER and MOORE), T., 1109.

37 III

C_8H_9ON Ergotoxine ethyl ester, phosphate and hydrochloride of (BARGER and EWINS), T., 286; P., 2.

C₃₈ Group.

$C_8H_9ON_3$ Diazoamine, from ammonia and benzoylethyl-1:4-naphthylenediamine diazonium salts (MORGAN and COUZENS), T., 1696.

38 V

$C_{10}H_{15}O_2N_2SSi$ Cinchonidine *dl.* and *L*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 760.

C₃₉ Group.

$C_{10}H_{15}O_2N_2SSi$ Quinine *dl.* and *L*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 760.

$C_{10}H_{15}O_2N_2SSi$ *L*-Menthylamine dibenzylethylpropylsilicanedisulphonate (CHALLENGER and KIPPING), T., 153.

C₄₀ Group.

$C_{10}H_{15}O_2N_2SSi$ Strychnine *dl*-dibenzylethylpropylsilicanesulphonate and $\cdot 3H_2O$ (CHALLENGER and KIPPING), T., 150.

Strychnine *L*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 770.

C₁₂ Group.

$C_8H_5O_2$ Incarnatyl hydrogen phthalate, sodium salt of (ROGERSON), T., 1011.

42 IV

$C_{10}H_9O_2N_2S$ Bisphenetoleazosulphobenzylidenabenzidine, potassium salt (GREEN and SEX), T., 2247.

42 V

$C_{10}H_9O_2N_2SSi$ Brucine *dl.*, *D.* and *L*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 766.

C₄₄ Group.

$C_{10}H_9O_2N_2$ *o*, *pp'*-Tetrabenzoyloxy-2:5-diphenylpyrazine (TITIN), T., 2516.

$C_{10}H_9O_2N_2$ *d.* and *L*-Pavine *d*-tartrates (POLE and GIBSON), T., 2217.

C₅₄ Group.

$C_{10}H_9O_2N_2S$ Benzene-1:3:5-trisulphonylter-*p*-aminobenzeneazo- β -naphthol (MORGAN and PICKARD), T., 56.

C₆₀ Group.

C₆₀H₁₇O₁₆N₃Br₂S₂ *dl*-Pavine *dl*- α -bromo-camphor- π -sulphonate (H₂O, (POPE and GIBSON), T., 2210.

C₆₁ Group.

C₆₁H₇O₁₀N₃Si Strychnine dibenzylethylpropylsilicanedisulphonate (CHALLENGER and KIPPING), T., 151.

C₆₇ Group.

C₆₇H₃₆O₁₈ Benzoylcarthamine (KAMETAKA and PERRIN), T., 1421; P., 181.

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| Page | Line | |
|-------|----------------|--|
| 55 | 19 | for " $C_{24}H_{27}O_4N_4S_3$ " read " $C_{24}H_{29}O_6N_6S_2$." |
| 56 | 10 | " " $C_{24}H_{28}O_6N_6S_3$ " read " $C_{24}H_{29}O_6N_6S_3$." |
| 60 | 13* | " " $C_{13}H_{26}O_6N_6S_2$ " read " $C_{13}H_{26}O_6N_6S_2$." |
| 82 | 1 | " "3:6-Dibenzoyl-9-phenylanthracene" read "3:6-Dibenzoyl-9-phenylanthracene." |
| 464 | 2* | " " $C_{22}H_{27}O_2NS$ " read " $C_{22}H_{27}O_2NS$." |
| 690 | 12 | " " $C_{15}H_8O_2Cl_2$ " read " $C_{15}H_8O_2Cl_2$." |
| 1032 | 16, 6* | " "2-Methyl-1:3-benzoxazine 4-one" read "2-Methyl-1:3-dihydrobenzoxazine 4-one." |
| 1033 | 4, 11, 8*, 15* | " "2-Methyl-1:3-dihydrobenzoxazine 4-one." |
| 1056 | 10* | alter formula to " $N_3CH < \begin{smallmatrix} N \\ N \end{smallmatrix}$ " |
| 1219) | | |
| 1221) | | |
| 1223) | | in head-line for "NITROGEN" read "HYDROGEN." |
| 1225) | | |
| 1245 | 5 | for $\begin{array}{c} CH_2CCH_2CH_2 \\ \\ C-CH_2 \end{array}$ read $\begin{array}{c} CH_2CCH_2CH_2 \\ \quad \\ O \quad CO \end{array}$ |
| 1297 | 13* | " " $C_8H_4 < \begin{smallmatrix} CO \\ S \end{smallmatrix} > C_8H_4OH$ " read " $C_8H_4 < \begin{smallmatrix} CO \\ S \end{smallmatrix} > C_8H_4OH$." |
| 1398 | 4* | " "8-Nitro-6:7-dimethylcoumarin" read "5-Nitro-6:7-dimethylcoumarin." |
| 1733 | 20 | " "270°8" read "240°8." |
| 1738 | 11* | " "Benzoylnaphthoyl" read "Benzoyl." |
| 1826 | 2* | " "deep orange" read "pale yellow." |
| 2001 | 25 | " "has" read "have." |
| 2274 | 16* | " "3-Methyl." read "2-Methyl." |
| 2274 | 15* | " " $C_8H_4 < \begin{smallmatrix} CHMe \\ CO \end{smallmatrix} > CHCO_2Et$ " read " $C_8H_4 < \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} > CMeCO_2Et$." |
| 2275 | 1 | " "3-methyl." read "2-methyl." |
| 2275 | 10 | " "3-Methyl." read "2-Methyl." |
| 2275 | 10 | " " $C_6H_3 < \begin{smallmatrix} CHMe \\ CO \end{smallmatrix} > CH_2$ " read " $C_6H_3 < \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} > CHMe$." |
| 2275 | 11 | " "3-methyl." read "2-methyl." |

* From bottom.

Organic Chemistry.

Relation between the Specific Gravity and Optical Constants of Isomeric Organic Compounds. K. HEYDRICH (*Zeitsch. Kryst. Min.*, 1910, 48, 243—305).—The crystallographic constants, specific gravity, and refractive indices were determined for the following: Methyl oxalate (monoclinic, $a:b:c=1.0351:1.03346$; $\beta=101^\circ55'$, $D=1.422$. Refractive indices for D line [values for C and F lines are also given for each of the compounds], $a=1.4177$, $\beta=1.4616$, $\gamma=1.5521$). Succinic acid (monoclinic, $a:b:c=0.5688:1.06195$; $\beta=91^\circ20'$, $D=1.562$ — 1.567 , $a=1.4503$, $\beta=1.5338$, $\gamma=1.6100$). Catechol (monoclinic, $a:b:c=1.6086:1.10229$; $\beta=94^\circ15'$, $D=1.567$ — 1.375 , $a=1.595$, $\beta=1.609$, $\gamma=1.747$). Resorcinol (orthorhombic, $a:b:c=0.9110:1.0549$, $D=1.281$ — 1.285 , $a=1.5781$, $\beta=1.6197$, $\gamma=1.6273$). Quinol (ditrigonal-scalenohedral, $a:c=1.06680$, $D=1.328$ — 1.332 , $\omega=1.6325$, $\epsilon=1.6262$). 2:4-Dinitrotoluene (monoclinic, $a:b:c=0.85930:1.054076$; $\beta=94^\circ18'$, $D=1.518$ — 1.521 , $a=1.4423$, $\beta=1.6619$, $\gamma=1.7556$). 2:6-Dinitrotoluene (orthorhombic, $a:b:c=0.5714:1.05407$, $D=1.538$ — 1.540 , $a=1.4788$, $\beta=1.6694$, $\gamma=1.7244$). Codeine (orthorhombic, $a:b:c=0.9595:1.08346$, $D=1.309$ — 1.315 , $a=1.5428$, $\beta=1.6355$, $\gamma=1.6838$). isoCodeine (orthorhombic, $a:b:c=0.6322:1.05600$, $D=1.361$ — 1.367 , $a=1.4679$, $\beta=1.6422$, $\gamma=1.6754$). ψ -Codeine (monoclinic, $a:b:c=2.1042:1.1036$; $\beta=108^\circ14'$, $D=1.288$ — 1.290 , $a=1.5743$, $\beta=1.6021$, $\gamma=1.6472$). Dicyanodiamide (monoclinic, $a:b:c=1.1109:1.14213$; $\beta=115^\circ20'$, $D=1.404$ — 1.405 , $a=1.5212$, $\beta=1.5493$, $\gamma=1.8471$). Melamine (monoclinic, $a:b:c=1.4121:1.09728$; $\beta=112^\circ16'$, $D=1.573$, $a=1.4906$, $\beta=1.7429$, $\gamma=1.8731$). Potassium phenol- o -sulphonate (orthorhombic, $a:b:c=0.7796:1.04621$, $D=1.733$ — 1.734 , $a=1.5263$, $\beta=1.5677$, $\gamma=1.6467$). Potassium phenol- p -sulphonate (orthorhombic, $a:b:c=0.8790:1.10017$, $D=1.869$ — 1.871 , $a=1.5714$, $\beta=1.6079$, $\gamma=1.6942$).

In each of these isomeric groups an increase in sp. gr. is accompanied by an increase in the mean refractive index, the specific refractive power remaining practically the same. For the polymeric substances there is a much greater difference in the specific refractive power.

L. J. S.

Hydrocarbons of the Wool Grease Oleins. I. AUGUSTUS L. GILL and LAURENCE R. FORREST (*J. Amer. Chem. Soc.*, 1910, 32, 971—1073).—The hydrocarbons obtained by the hydrolysis of distilled wool grease oleins were freed from cholesterol and fractionally distilled under 1 mm. pressure. Each fraction was crystallised from acetone, so that the material was finally divided into two series of ethylene hydrocarbons; the first, containing twelve terms soluble in acetone at 0° , ranged from heptadecylene to triacontylene, $C_{30}H_{60}$, whilst the insoluble series included nine members, from eicosylene,

$C_{20}H_{40}$, to nonacosylene, $C_{29}H_{58}$. The b. p., molecular weight, and iodine number of each fraction is given. W. O. W.

Historical Notes on C-Nitroso-compounds. EUGEN BERGER (*Ber.*, 1910, 43, 2353—2355. Compare Abstr., 1900, i, 500). —The following arguments are brought forward against Piloty's formula, $CMe_2:NO \cdot O \cdot NO$, for ψ -nitroles (*Ber.*, 1902, 35, 3094 note).

(1) In all cases in which the hydrogen atom of the $:NO \cdot OH$ group of nitronic acid is replaced, the substituent becomes attached to carbon, for example, $CHMe:NO \cdot OH$ gives $CH_3 \cdot CHBr \cdot NO_2$. (2) A nitrite of the type $CMe_2:NO \cdot O \cdot NO$, should be readily hydrolysed by water; ψ -nitroles are not. (3) Piloty's formula does not account in any way for the similarity between ψ -nitroles and true C-nitroso-compounds. J. J. S.

Action of Grignard's Reagents on Methyl ethylacetaldehyde and the Preparation of Certain Diolefines. F. BJELOUSS (*Ber.*, 1910, 43, 2330—2333). —A series of unsaturated secondary alcohols has been prepared by the action of magnesium ethyl, isobutyl, and isoamyl bromides on methyl ethylacetaldehyde, and these alcohols have been transformed into diolefines containing conjugate double linkings by means of crystallised oxalic acid (Zelinsky, Abstr., 1902, i, 2).

δ -Methyl- Δ^7 -hepten- ϵ -ol, $CH_3Et \cdot CMe \cdot CH_2Et \cdot OH$, prepared from ethyl magnesium bromide and methyl ethylacetaldehyde, is a colourless liquid with a strong odour, and has b. p. $103-104^\circ/75$ mm., D_4^{25} 0.8545, and n_D^{25} 1.44436. The acetate, $C_{10}H_{18}O_2$, has b. p. $113^\circ/80$ mm., and the chloride, $C_8H_{15}Cl$, b. p. $75-78^\circ/53$ mm. $\delta\eta$ -Dimethyl- Δ^7 -octen- ϵ -ol, $CH_3Et \cdot CMe \cdot CH(OH) \cdot CH_2 \cdot CHMe_2$, is a colourless, mobile liquid, b. p. $108-111^\circ/40$ mm. It has D_4^{25} 0.8444 and n_D^{25} 1.44503. The acetate, $C_{12}H_{22}O_2$, has b. p. $103-105^\circ/20$ mm., and the chloride, $C_{10}H_{19}Cl$, b. p. $76-79^\circ/13$ mm.

$\delta\theta$ -Dimethyl- Δ^7 -nonen- ϵ -ol, $CH_3Et \cdot CMe \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CHMe_2$, has b. p. $110-112^\circ/19$ mm., D_4^{25} 0.8441, and n_D^{25} 1.44782. The acetate, $C_{13}H_{24}O_2$, has b. p. $122-125^\circ/31$ mm., and the chloride, $C_{11}H_{21}Cl$, b. p. $93-95^\circ/18$ mm., but evolves hydrogen chloride.

δ -Methyl- Δ^6 -heptadiene, $CH_3Et \cdot CMe \cdot CH \cdot CHMe$, is a colourless, mobile liquid, b. p. $131-132^\circ$. It has D_4^{25} 0.7551 and n_D^{25} 1.46211, and shows the usual exaltation.

$\beta\epsilon$ -Dimethyl- Δ^7 -octadiene, $CH_3Et \cdot CMe \cdot CH \cdot CH \cdot CHMe_2$, has b. p. 165° , D_4^{25} 0.7754, and n_D^{25} 1.46136.

$\delta\theta$ -Dimethyl- Δ^7 -nonadiene, $CH_3Et \cdot CMe \cdot CH \cdot CH \cdot CH_2 \cdot CHMe_2$, has b. p. $185-189^\circ$, D_4^{25} 0.7779, and n_D^{25} 1.46189. J. J. S.

Preparation of Keto-alcohols. FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.P. 223207). —The condensation products of ketones and alcohols have previously been described (compare Abstr., 1905, i, 443, 732); when this reaction is carried out in the presence of alkali carbonates or hydroxides, it yields stable compounds of therapeutic value.

Methyl hydroxyethyl ketone, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH$, a colourless,

odourless oil, miscible with water, alcohol, or ether in all proportions, b. p. 109—110°/30 mm., is prepared by treating acetone (3 parts) with 35% formaldehyde solution (1 part), slowly adding potassium carbonate, heating to 30—35°, and subsequently distilling the acidified solution in a vacuum. The acetate is a colourless oil, b. p. 96°/15 mm.

Methyl β-hydroxyisopropyl ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, a viscous, colourless oil, b. p. 90—95°/15 mm., is prepared in similar manner from methyl ethyl ketone.

F. M. G. M.

The Fatty Acids. S. FACHINI and G. DORTA (*Boll. chim. farm.*, 1910, 49, 237—247).—The authors base a method for the separation of the solid fatty acids from the liquid and unsaturated fatty acids on the sparing solubility of the former in light petroleum of low boiling point (30—50°). Solutions of stearic, palmitic, and myristic acids in this solvent deposit the whole of the dissolved substance when cooled to -40° in alcohol and solid carbon dioxide. Lauric acid is somewhat more soluble. The separation of the above acids on cooling is also almost quantitative even when the solution contains liquid fatty acids. It cases where large amounts of the former are present in the mixture, it is advisable first to remove the greater part of them from the solution by moderate cooling, and subsequently to precipitate the rest at -40°. This procedure facilitates filtration. The method is conveniently employed for the separation of arachidic acid, which crystallises along with lignoceric acid when the fatty acids from arachis oil are treated in the manner indicated.

R. V. S.

Mixed Anhydrides. ENOS FERRARIO (*Gazzetta*, 1910, 40, ii, 95—100).—The method of preparation of benzoyl nitrate by the action of benzoyl chloride and silver nitrate (Francis, *Trans.*, 1906, 89, 1) may be applied to other organic nitrates, and also to nitrites.

Acetyl nitrite, $\text{CH}_3\cdot\text{CO}\cdot\text{NO}_2$, is prepared by the action of acetyl chloride on dry silver nitrite at -30° to -40°. It is finally distilled at 45° in carbon dioxide. For the purpose of estimating the nitrogen, the vapours are passed, mixed with carbon dioxide, over a heated copper spiral. Propionyl, butyryl, and benzoyl nitrites are prepared in similar manner. The nitrites obtained are identical with those prepared by Francesconi and Cialdea (*Abstr.*, 1904, i, 707) by the action of nitrosyl chloride on silver salts.

C. H. D.

Preparation of Derivatives of ββ-Dialkylpropionic Acids. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 222809).—It is found that the derivatives of ββ-dialkylpropionic acids of the general formula $\text{CHR}_1\text{R}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (where R_1 and R_2 are alkyl radicles) have with the exception of the methyl and ethyl derivatives valuable therapeutic properties, and are quite tasteless.

β-Ethylvaleryl chloride, b. p. 150—155°, prepared from β-ethylvaleric acid and phosphorus pentachloride, yields when treated with ammonium hydroxide, *β-ethylvalerylamide*, m. p. 127.5°; the *carbamide*, m. p. 197°, is prepared in the usual manner.

Menthyl β-ethylvalerate, b. p. 155°/12 mm., is obtained by the action of the foregoing chloride on menthol in the presence of pyridine.

F. M. G. M.

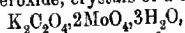
Glucinum Lactate. G. CALCAONI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 229—233, 290—293).—From glucinum carbonate and lactic acid a salt of the composition $\text{Gl}_2(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 19\text{H}_2\text{O}$ can be obtained, but it is not a chemical individual, for when its aqueous solution is fractionally precipitated with alcohol, precipitates of various compositions are obtained. Indirectly, however, indications were obtained of the existence of salts of compositions other than those studied by previous authors. The specific conductivity of a solution of lactic acid to which glucinum oxide is added at first decreases, then increases rapidly until one half the molecular quantity of the oxide is present. The conductivity then rises, but very slightly, reaching a maximum when the molecular quantity of glucinum oxide has been added. Further addition of glucinum oxide causes a decrease in conductivity. These results are obtained at all degrees of dilution, and analogous behaviour is observed when the depression of the freezing point of the solution is measured. Hence it is probable that in addition to the normal salt which has been supposed to exist, another is formed composed of equimolecular quantities of base and acid. Above the concentration corresponding with this salt, glucinum oxide dissolves in the solution without forming salts, and its presence modifies the nature of the solvent, so that the conductivity and freezing point of the solvent are lowered (compare Parsons, Robinson, and Fuller, *Abstr.*, 1908, ii, 105).
R. V. S.

Action of Sodium Alkylloxides on Ethyl Acetoacetate. TELEMACHOS KOMNENOS (*Monatsh.*, 1910, 31, 687—693. Compare this vol., i, 361).—By the interaction of sodium methoxide and ethyl acetoacetate in methyl-alcoholic solution a practically quantitative yield of methyl acetoacetate can be obtained. When sodium amylxide and amyl alcohol are used, amyl acetoacetate is obtained. The formation of ethyl acetoacetate from sodium ethoxide and methyl acetoacetate in ethyl-alcoholic solution also takes place readily.

In the distillation of methyl acetoacetate there is no formation of dehydracetic acid, but the latter is formed in large quantity when amyl acetoacetate is distilled, and the author recommends this as the best method of preparation.
T. S. P.

Oxo-salts of Molybdenum. ARRIGO MAZZUCHELLI and G. ZANGRILLI (*Gazzetta*, 1910, 40, ii, 49—73).—It has been shown (*Abstr.*, 1907, i, 748) that molybdenum peroxide is capable of forming a complex oxalate. A number of similar salts have now been examined.

The addition of hydrogen peroxide to a solution of ammonium molybdenum oxalate yields a yellow solution, which deposits crystals of a salt, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{MoO}_4$. When dilute solutions are used, a product containing a smaller proportion of oxygen is obtained. The potassium salt, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{MoO}_4$, forms yellow crystals. If finely powdered and shaken with hydrogen peroxide, crystals of a salt,



separate, and an orange ammonium salt of corresponding composition has been obtained. The sodium salt, precipitated by alcohol, has the

composition $\text{Na}_2\text{C}_2\text{O}_4\cdot\text{Mo}_2\text{O}_7$, probably owing to hydrolysis. Potassium molybdoiodate yields only an amorphous product on oxidation, and ammonium molybdophosphate yields a product which does not contain active oxygen.

Potassium molybdoarsenate and hydrogen peroxide yield only a potassium ozomolybdate, $\text{K}_2\text{MoO}_5\cdot 3\text{H}_2\text{O}$, free from arsenic.

Cryo-copic measurements have been made, using solutions of various complex salts and acids of molybdenum, and adding successive quantities of hydrogen peroxide. The results show that the number of molecules present in the solution is not increased by such additions until the ratio $\text{H}_2\text{O}_2:\text{MoO}_3$ is reached, and it appears that even a further quantity enters into combination. Such a salt as $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{MoO}_3$ may exist, the salt KVO_3 being already known.

The results are, however, complicated by a decomposition of the complex salts, and do not admit of any simple interpretation. Measurements with methyl molybdate have also been made as a means of determining the molecular complexity.

C. H. D.

Synthesis of the $\alpha\delta$ -Dimethyladipic Acids and Separation of the Racemic Acid into Optical Isomerides. WILLIAM A. NOYES and L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1910, 32, 1057—1061).—Lean has expressed the view that the carbon atoms in $\alpha\beta$ -dialkylsuccinic acids and similar compounds are so united that optical isomerism is impossible (*Trans.*, 1894, 65, 1001). That this is not the case is now shown by the resolution of $\alpha\delta$ -dimethyladipic acid through the agency of its acid brucine salts. *d- $\alpha\delta$ -Dimethyladipic acid*, m. p. 104—105°, has $[\alpha]_D^{25} + 31.3^\circ$ in 10% alcoholic solution. The *l*-form was obtained in an impure condition, having $[\alpha]_D - 23.4^\circ$. Attempts to resolve the meso-form were unsuccessful.

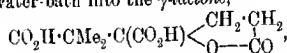
The preparation of $\alpha\delta$ -dimethyladipic acid is considerably facilitated by substituting magnesium amalgam (Meunier, *Abstr.*, 1904, i, 7) for sodium in the condensation of ethylene dibromide with ethyl malonate.

W. O. W.

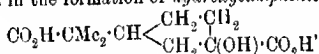
Camphenic (Camphenecamphoric) Acid. OSSIAN ASCHAN (*Annalen*, 1910, 375, 336—378).—Camphenic acid (the name is proposed by the author for camphenecamphoric acid) constitutes about 70% of the total oxidation products of camphene, whether natural or artificial, by alkaline potassium permanganate. In support of the annexed formula, the following facts are stated. Camphenic acid, $\text{C}_8\text{H}_{14}(\text{CO}_2\text{H})_2$, m. p. 135.5—136.5°, is a saturated, monocyclic dicarboxylic acid which does not form an anhydride.

It is a racemic compound, the active forms being optical antipodes, $[\alpha]_D \pm 1.8^\circ$, m. p. 143—144°; the *l*-form has been obtained by Wallach and Gutmann (*Abstr.*, 1907, i, 1061), and the *d*-form by the author by the oxidation of a highly dextrorotatory camphene prepared from Grecian turpentine. Like camphoric acid, camphenic acid is converted by glacial acetic acid and hydrochloric acid, D 1.2, at 180° into an *isomeride* (trans-form?), which, however, could not be isolated in a pure state (the separation of the two isomeric

acids has since been accomplished by Wallach). Camphenic acid (1 mol.) is treated with phosphorus pentachloride (2 mols.), and, after the cessation of the reaction, with bromine (rather more than 1 mol.) in the cold, whereby under conditions detailed by the author *α-bromo-camphenic acid*, $C_8H_{13}Br(CO_2H)$, m. p. 190° , is obtained; only 1 atom of the halogen can be introduced smoothly. When bromo-camphenic acid is heated with a solution of sodium carbonate on the water-bath for about fifteen minutes, it is partly converted into *dehydrocamphenic acid*, m. p. 155° , which receives the constitution $CO_2H \cdot CMe_2 \cdot CH \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot C \cdot CO_2H \end{smallmatrix}$, because it is converted by nitric acid, D 1252, on the water-bath into the *γ-lactone*,



m. p. 254° (decomp.). The decomposition of the lactone by fusion with potassium hydroxide yields chiefly *isobutyric acid*, together with succinic and oxalic acids. The action of sodium carbonate on bromocamphenic acid also results in the formation of *hydroxycamphenic acid*,

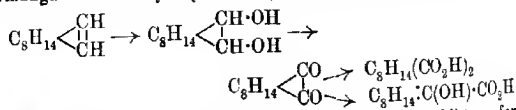


m. p. 152° , which is stable to potassium permanganate, and is not affected by 40% sulphuric acid on the water-bath, thus proving that the hydroxyl group is not in the *γ*-position to a carboxyl group.

Whilst bringing forward the preceding constitution of camphenic acid with reserve, the author claims that much can be said in favour of the annexed constitution of camphene. Touching on the vexed question of the nature of camphene, the author

is disinclined to accept Moycho and Zienkowski's suggestion of its dual character (Abstr., 1904, i, 438; 1905, i, 710), but leans to Semmler's view of its homogeneity. Nevertheless, in consequence of the

large percentage of camphenic acid obtained by the oxidation of camphene, he rejects Wagner's "methylene" formula of camphene (which necessitates the assumption of the formation of several intermediate substances in order to explain the formation of camphenic acid) and proposes the "ethylene" formula given above. Certainly Wagner's claim that the camphenic acid is produced from the immediately formed camphenylic acid must be wrong, because, as the author shows, the latter does not yield camphenic acid when oxidised by potassium permanganate. The formation of camphenic and camphenylic acids by the oxidation of camphene by alkaline potassium permanganate is easily explicable by the author's formula:



the camphenylic acid being produced by a "benzylic acid" transformation in manner quite analogous to the formation of *β-fenchocarboxylic acid* from carbofenchone.

C. S.

New Formation of Carboxylic Acids of the Carbohydrates. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, 28, 355—358).—By the oxidation of dextrose with nitric acid (D 1.15) in addition to saccharic acid, a *carboxylic acid*, $\text{CHO} \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CO}_2\text{H}$, identical or isomeric with glycronic acid is formed. The *barium* salt, a colourless powder, and the free acid both strongly reduce Fehling's solution, give an intense colour reaction with naphthaborescinol, and also show positive phloroglucinol and orcinol tests. Barium hydroxide produces a precipitate of an orange-coloured, flocculent basic salt. A furfuraldehyde distillation showed the conversion of 10 per cent. of the original dextrose into this form.

E. F. A.

Carbithionic Acids. IV. Esters of Perthioacetic, -propionic, and phenylacetic Acids. JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1910, 43, 2481—2485. Compare Abstr., 1907, i, 382, 474).—*Methyl dithioacetate*, $\text{CH}_3 \cdot \text{CS} \cdot \text{SMe}$, is prepared by the interaction of magnesium methyl iodide with carbon disulphide, treatment of the reaction mixture with ice, followed by the addition of ammonium chloride. The carbithionate is shaken with methyl sulphate, when a red oil separates, which is distilled with steam to destroy excess of methyl sulphate. The ester is a reddish-yellow oil, b. p. 80—81°/95 mm., 71.70 mm., 142°/760 mm., D_4^{20} 1.096; it has a characteristic odour.

Methyl dithiopropionate, $\text{CH}_2\text{Me} \cdot \text{CS} \cdot \text{SMe}$, is a reddish-yellow oil, b. p. 92—93°/70 mm., 47°/11 mm., 159—160°/760 mm., D_4^{20} 1.047.

Methyl dithiophenylacetate, $\text{CH}_2\text{Ph} \cdot \text{CS} \cdot \text{SMe}$, is a reddish-yellow oil of characteristic odour, b. p. 149°/12 mm., 280°/760 mm. (decomp.), D_4^{20} 1.1389.

E. F. A.

Hyposulphites. VIII. Aldehydesulphoxylates and Potassium Cyanide. ARTHUR BINZ and TH. MARX (*Ber.*, 1910, 43, 2350—2352. Compare Binz, Abstr., 1909, ii, 229).—Neither rongalite nor potassium cyanide alone reduces indigocarmin in the cold, whereas a mixture of the two does. It is also shown that potassium cyanide accelerates the reducing power of rongalite towards indican, whereas it has no such effect on benzaldehydesulphoxylate.

The effects are probably catalytic. The reaction with indigocarmin is of interest, as it belongs to the group of reactions which take place only after the lapse of a certain time.

J. J. S.

Dissociation Processes in the Sugar Group. II. Behaviour of Carbohydrates towards Alkali Hydroxides. JOHN U. NEF (*Annalen*, 1910, 378, 1—119. Compare Abstr., 1905, i, 3; 1908, i, 5).—Twenty-four isomeric saccharinic acids with six carbon atoms are possible, namely, eight stereoisomeric *metasaccharinic* acids ($\alpha\gamma\delta\epsilon$ -tetrahydroxhexoic acids), $\text{CO}_2\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, derived from the sixteen aldohexoses; four stereoisomeric *isosaccharinic* acids ($\alpha\gamma\delta$ -trihydroxy- α -hydroxymethylvaleric acids),

$\text{CO}_2\text{H} \cdot \text{C}(\text{OH})[\text{CH}_2(\text{OH})] \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, derived from the eight β -ketoheptoses; eight saccharinic acids ($\alpha\beta\gamma\delta$ -tetrahydroxy- α -methylvaleric acids),

$\text{CO}_2\text{H} \cdot \text{CMe}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$; and four *parasaccharinic* acids ($\alpha\beta\gamma$ -trihydroxy- $\alpha(\omega)$ -hydroxyethyl.

butyric acids), $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$. The eight saccharinic acids are formed from the eight 3-ketohexoses, but the *parasaccharinic* acids are not obtained by the action of alkali hydroxides. Hence the number of possible C_6 saccharinic acids derived from the thirty-two different hexoses is theoretically twenty isomerides.

In the case of all carbohydrates, whether aldoses or ketoses, and irrespective of the number of carbon atoms, the salt formation with alkali hydroxides takes place at the carbon atom next the carbonyl group, $-\text{CH}(\text{OH})\cdot\text{CH}(\text{OM})\cdot\text{CO}-$. The methylene derivative,

$$-\text{CH}(\text{OH})\cdot\overset{\text{A}}{\text{C}}\cdot\text{CO}-,$$

in the absence of an oxidising agent undergoes rearrangement to

$-\text{CH}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot\text{CO}-$, and this to *ortho*-osone, $-\text{CH}_2\cdot\text{CO}\cdot\text{CO}-$, from
glycide, $\begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array}$, and this to *ortho*-osone, $-\text{CH}_2\cdot\text{CO}\cdot\text{CO}-$, from

which by the benzilic acid transformation saccharinic acids are formed. In the presence of an oxidising agent, oxygen is absorbed, and the 1:2-osone, $-\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CO}-$, is formed. Enzymes act in a similar manner on the carbohydrates, but their barely basic nature does not bring about the transformation of the *ortho*-osones formed into saccharinic acids.

Similarly, four C_4 saccharinic acids are derived from the six isomeric tetroses, and ten C_5 saccharinic acids from the fifteen isomeric pentoses; in the following the two α -dihydroxybutyric acids, the four α -tri-hydroxyvaleric acids, and α - and β -dextrometasaccharinic acids are described.

Hexoses decompose into a molecule each of diose and aldotetrose, or into 2 molecules of glyceraldehyde; the decomposition into formaldehyde and an aldopentose has never been observed. In nature, pentoses are never formed by the degradation of hexoses; hexoses are never built up from pentoses and formaldehyde. Pentoses form α,β -dienols, $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot(\text{CH}\cdot\text{OH})_2\cdot\text{CH}_2\cdot\text{OH}$, which in the main give aldotetroses and hydroxymethylene; to some slight extent they form β -dienols, $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which decompose into diose and glyceraldehyde. Dextroses exclusively form 2:3-dienols, and decompose into 2 molecules of diose; they never form hydroxymethylene and glyceraldehyde.

When hexoses or pentoses are treated with 8*N*-sodium hydroxide, only the C_6 or C_5 saccharinic acids of the corresponding series are formed, as the products of decomposition (hydroxymethylene, diose, glyceraldehyde, and aldotetrose) do not under these conditions undergo synthetic condensation to every possible hexose and pentose. Hydroxymethylene, however, forms the dienol, $\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})$; this changes into glycolaldehyde, $\text{CH}_2(\text{OH})\cdot\text{CHO}$, which condenses exclusively to tetrose, from which *d*- and *l*- α -dihydroxybutyric acids are formed. It is not certain whether glyceraldehyde in the same manner gives exclusively *d*- and *l*-lactic acids.

When dilute sodium hydroxide is used, a mixture of every possible saccharinic acid with three, four, five, or six carbon atoms is obtained. This is the case when sparingly soluble metallic hydroxides, such as those of calcium and barium, are used. With 8*N*-sodium hydroxide the

pentoses give only six saccharinic acids, and hexoses only eight, namely, *D*- and *L*-lactic acids, *D* and *L*- α -dihydroxybutyric acids, and two *meta*- and two *iso*-saccharinic acids with six carbon atoms.

I. *L*-Arabinose and 8*N*-sodium hydroxide; 100 grams of sugar yield about 80 grams of non-volatile saccharinic acids, together with more or less of a dark reddish-brown, neutral resin soluble in water; this is chiefly formed from diose. After a lengthy process of separation, for the details of which the original must be consulted, *D*-*threo*- α - δ -

trihydroxyvaleric acid, $\text{CO}_2\text{H}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{CH}_2\cdot\text{OH}$, and *L*-*erythro*- α - δ -*trihydroxyvaleric acid*, $\text{CO}_2\text{H}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{CH}_2\cdot\text{OH}$, were isolated.

The *quinine* salt of the former crystallises in lustrous needles, m. p. 172°, $[\alpha]_D^{20} - 103.3^\circ$. The *phenylhydrazide* forms voluminous, colourless needles, m. p. 110°, $[\alpha]_D + 26.36^\circ$. The *brucine* salt separates in flat, lustrous prisms, $[\alpha]_D^{20} - 18.77^\circ$; the *sodium* salt has $[\alpha]_D^{20} + 23.76^\circ$.

D-*threo*- α - δ -*dihydroxyvalerolactone* is a colourless, mobile oil, $[\alpha]_D - 36.5^\circ$; it is oxidised by dilute nitric acid to *D*- α -*dihydroxy-diglytaric acid*, m. p. 135°, $[\alpha]_D^{20} - 2.6^\circ$; the *disodium* salt has $[\alpha]_D^{20} + 22.25^\circ$.

L-*Erythro-trihydroxyvaleric acid* forms a *phenylhydrazide*, crystallising in colourless, concentrically-grouped, dense needles, m. p. 145–150°, $[\alpha]_D^{20} - 8.93^\circ$. The *lactone* has $[\alpha]_D^{20} - 45^\circ$ to -55° .

D- α -*Dihydroxybutyric acid* forms a *brucine* salt, m. p. 188° (decomp.), $[\alpha]_D^{20} - 27.23^\circ$, and a *phenylhydrazide*, crystallising in needles, m. p. 130–131°; on oxidation, *DL*-malic acid is formed.

DL- β -*Dihydroxybutyric acid* yields a *phenylhydrazide*, m. p. 99°.

DL- α -*Dihydroxybutyric acid* can be resolved by means of *brucine*. The *brucine* salt of the *D*-isomeride had m. p. 188° (decomp.), $[\alpha]_D^{20} - 20.1^\circ$, the free acid having $[\alpha]_D + 20^\circ$ (about); it yields *D*-malic acid on oxidation.

II. Glycolaldehyde and strong sodium hydroxide form a good deal of resin and traces of formic acid, the main product being *DL*- α -hydroxybutyrolactone. No trace of *DL*-lactic acid is formed.

III. *L*-Xylose with 8*N*-sodium hydroxide yields *L*-*threo*- and *D*-*erythro*-*trihydroxyvaleric acids*, the antipodes of those given by *L*-arabinose. The *quinine* salts of these two acids crystallise together, m. p. 165°, $[\alpha]_D - 113.2^\circ$; that of the *D*-*erythro*- α - δ -*trihydroxyvaleric acid* forms lustrous needles, m. p. 172°, $[\alpha]_D - 10.1^\circ$. The *phenylhydrazide* has m. p. 150°, $[\alpha]_D^{20} + 9.38^\circ$.

L-*threo*- α - δ -*trihydroxyvaleric acid* forms a *brucine* salt, crystallising in transparent, concentrically-grouped, flat prisms, m. p. 145–150°, $[\alpha]_D^{20} - 34.67^\circ$; a *quinine* salt, separating in needles, m. p. 160–162°, $[\alpha]_D^{20} - 119.45^\circ$; a *phenylhydrazide*, crystallising in colourless needles, m. p. 110–112°, $[\alpha]_D^{20} - 25.43^\circ$, and a *lactone*, $[\alpha]_D^{20} + 42.5^\circ$.

DL-*threo*- α - δ -*trihydroxyvaleric acid phenylhydrazide*, prepared by the union of the antipodes, crystallises in needles, m. p. 128–130°, and is a true racemate.

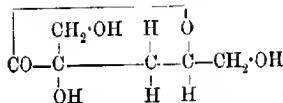
IV. *d*-Galactose with 8*N*-sodium hydroxide yields much less *dl*-lactic acid than dextrose, but, on the other hand, far more *dl*- α -dihydroxy-butyric acid.

The compound previously described (Abstr., 1908, i, 8) as giving brucine *dl*-parasaccharinate, m. p. 193—194°, is in reality *dl*- α -hydroxy-butyrolactone.

*meta*Saccharin and *parasaccharin* are stereoisomerides, and correspond with the α - and β -*d*-galactometasaccharinic acids. Accordingly, the four *parasaccharinic* acids disappear from the literature.

[With LUCAS]—The lactone of α -hydroxymethyl-*d*-lyxonic acid, prepared by the oxidation of an alkaline solution of galactose with air, forms crystals, m. p. 107—108°, $[\alpha]_D^{20} + 82.3^\circ$. The brucine salt crystallises in transparent, flat needles, m. p. 166°, $[\alpha]_D^{20} - 27.6^\circ$; the quinine salt has m. p. 162°, $[\alpha]_D^{20} - 107.5^\circ$; the phenylhydrazide has m. p. 162°, $[\alpha]_D^{20} - 11.06^\circ$. The levulosecarboxylic acid, prepared by the addition of hydrogen cyanide to levulose, has the formula of an α -hydroxymethyl-*d*-gluconic acid; apparently the addition of hydrogen cyanide is entirely asymmetric, as no isomeric levulosecarboxylic acid is formed.

α -*d*-isoSaccharin (annexed formula) crystallises in heavy, measurable crystals, m. p. 96°, $[\alpha]_D^{20} + 61.9^\circ$. Characteristic are the calcium and quinine salts described by Kiliani (Abstr., 1904, i, 373). The brucine salt forms pointed needles, m. p. 164°; the phenylhydrazide forms needles, m. p. 120—122°, $[\alpha]_D^{20} + 19.6^\circ$.



α -*d*-Galactometasaccharin (compare Kiliani, Abstr., 1905, i, 737) has m. p. 141°, $[\alpha]_D^{20} - 45.3^\circ$. The brucine salt forms transparent, hexagonal plates, m. p. 140°, $[\alpha]_D^{20} - 12.74^\circ$; the strychnine salt has decomp. 185—195°, $[\alpha]_D^{20} - 8.41^\circ$; the barium salt has $[\alpha]_D^{20} + 27.4^\circ$.

β -*d*-Galactometasaccharin (Kiliani's *parasaccharin*). The strychnine salt has m. p. 125—130°, $[\alpha]_D^{20} - 23^\circ$.

These α - and β -acids are related in the same manner as gluconic and mannonic acids, and are converted into one another on heating above 200°.

α -*d*-Galactometasaccharonic acid (Kiliani, Abstr., 1885, 745) has m. p. 155°, $[\alpha]_D^{20} + 22.25^\circ$. The disodium salt has $[\alpha]_D^{20} + 19.11^\circ$. The β -isomeride (Kiliani, Abstr., 1904, i, 373, 975) forms a lactone, m. p. 159—160°, $[\alpha]_D^{20} - 98.05^\circ$; the disodium salt has $[\alpha]_D^{20} - 18.23^\circ$.

These isomeric d - α , β -trihydroxyadipic acids are readily converted when heated with acetic anhydride into γ -hydroxymuconolactone, $\text{CH}_2\text{CH}(\text{CO}-\text{O})\text{C}:\text{CH}\cdot\text{CO}_2\text{H}$, which crystallises in transparent, yellow plates, m. p. 228—230°.

V. Dextrose with 8*N*-sodium hydroxide yields a considerable quantity of *dl*-lactic acid, and about 25% of saccharins, mainly α - and β -*d*-dextrometasaccharin, with relatively little isosaccharin. There is also but little resin produced.

β -Dextrometasaccharin, m. p. 92°, $[\alpha]_D^{20} + 8.2^\circ$, forms a sparingly soluble calcium salt, $[\alpha]_D^{20} - 23.25^\circ$, a brucine salt crystallising in long, transparent, rectangular plates or needles, decomp. 130—150°.

Hexose Phosphoric Acid Ester. A. VON LEBEDEF (Biochem. Zeitsch., 1910, 28, 213—229. Compare Abstr., 1909, i, 863).—The same hexose phosphoric acid ester is formed from dextrose and laevulose on fermentation with yeast juice. The compound with phenylhydrazine is considered to be the *phenylhydrazino-phosphoric acid* compound of a hexosazone, $C_{24}H_{31}O_7N_6P$, that is, $C_6H_8N_2 \cdot H_2PO_4 \cdot C_6H_5(OH)_3 \cdot (N_2HPh)_2$. It crystallises in canary-yellow bunches of needles of silky lustre, m. p. 148—150° (decomp.). When heated with hydrochloric acid, the corresponding *hexosone-phosphoric acid* ester is formed; it yields an amorphous, sparingly soluble *lead* salt. When heated with potassium hydroxide, the hydrazinohexosazone yields dextrosazone and glyoxal-osazone.

The hexose phosphoric ester forms a colourless, amorphous *phenylhydrazone*, also a *p-bromophenylhydrazone* crystallising in colourless needles, m. p. 128° (decomp.). The *p-bromophenylsazone* is yellow, m. p. 165°.

The ester is a compound of 1 mol. of carbohydrate and 1 mol. of phosphoric acid, which latter cannot be attached to the two terminal groups which react with phenylhydrazine. It is apparently different from the compound described by Young (Proc., 1907, 23, 65), and also differs from the glucophosphoric acid prepared by Neuberg and Pollak (this vol., i, 157, 610), which reacts with phenylhydrazine, forming glucosazone, and does not form a sparingly soluble phenylhydrazone.

E. F. A.

A Simple Method for the Preparation of Glucosamine Hydrochloride from Ovomucoid. ADOLF OSWALD (Zeitsch. physiol. Chem., 1910, 68, 173—180).—By warming ovomucoid for about an hour with 3% hydrochloric acid, glucosamine hydrochloride is obtained from the products by simply concentrating on the water-bath. It then crystallises out. Ovomucoid contains glucosamine as such, not as a polymeric product.

W. D. H.

Derivatives of Lactose and of Maltose and Two New Glucosides. EMIL FISCHER and HANS FISCHER (Ber., 1910, 43, 2521—2536).—The method of synthesising disaccharides by the interaction of " β -bromoacetodextrose" and silver carbonate (Fischer and Delbrück, Abstr., 1909, i, 633) has been applied to "*bromoacetolactose*" and "*bromoaceto-maltose*" with the expectation of obtaining tetrasaccharides. The hope has been partially fulfilled in the former case. A solution of "*bromoacetolactose*" in dry chloroform is shaken with freshly precipitated, dried silver carbonate, whereby a substance, $C_{24}H_{28}O_7(OAc)_{14}$, is obtained, which is probably the tetradeca-acetyl derivative of a tetrasaccharide; after purification by alcohol, it consists of a colourless, granular, indistinctly crystalline powder, which melts in boiling water. A sample, purified by shaking with dilute potassium hydroxide, has $[\alpha]_D^{20} + 20.69^\circ$ in chloroform. By hydrolysis in acetone with cold aqueous barium hydroxide, a substance is obtained, which, on account of its slight reducing action on Fehling's solution and the formation of a little phenyl-lactosazone with phenylhydrazine, is regarded as a mixture of about 25% of lactose (or of a substance which is easily converted into lactose) and a non-reducing carbo-

hydrate of high molecular weight, probably a tetrasaccharide; unfortunately, all attempts to obtain the latter in a pure state have been unsuccessful.

The interaction of "chloroacetomaltose" (or of the impure "bromoacetomaltose" described below) and freshly precipitated silver carbonate in moist ether yields *hepta-acetylmaltose*, $C_{36}H_{56}O_{13}$ m. p. 179–180° (corr.), which separates from alcohol in slender needles, strongly reduces warm Fehling's solution, and exhibits slight mutarotation, having $[\alpha]_D^{25} + 72.62^\circ$ to 76.66° in acetylene tetrachloride. From its method of formation it should be constituted similarly to hepta-acetyl-cellobiose (following abstract) and tetra-acetyldextrose, but it differs from these by its sparing solubility in dilute alkali.

The difficulty of obtaining crystallised "bromoacetomaltose" led the authors to examine the action of acetyl bromide on maltose. The direct interaction of the two substances, moderated by occasional cooling of the containing flask in a freezing mixture, yields a somewhat impure, amorphous bromohepta-acetylmaltose, which, however, can be used for the preceding and for the following experiment. *Hepta-acetylmenthylmaltoside*, $C_{36}H_{54}O_{13}$, m. p. 186° (corr.), obtained by shaking "bromoacetomaltose," dry silver carbonate, menthol, and ether for several hours, crystallises in needles, is odourless, does not reduce Fehling's solution, and has $[\alpha]_D^{25} + 20.84^\circ$ in *s*-tetrachloroethane. When its hot alcoholic solution is hydrolysed by boiling aqueous barium hydroxide, *menthylmaltoside*, $C_{22}H_{40}O_{11}$, m. p. 203° (corr.), $[\alpha]_D^{25} + 14.23^\circ$ in aqueous solution, is obtained, which separates from water in needles containing $2H_2O$, has an unpleasant taste, does not reduce Fehling's solution, and forms a *barium* salt, $(C_{22}H_{39}O_{11})_2Ba$.

The preparation of "bromoacetolactose" (bromohepta-acetyl-lactose) by Ditmar's method with acetyl bromide and dry lactose frequently miscarries from unknown causes. Therefore the authors employ the following very convenient method. A solution of octa-acetyl-lactose in acetic anhydride is treated with a saturated solution of hydrogen bromide in glacial acetic acid; after one hour and three-quarters at 15–26°, the mixture is poured into water at 0°, the precipitate is dissolved in chloroform, and is recovered by the addition of light petroleum to the washed and dried solution. By rapid crystallisation from warm alcohol the substance is obtained quite pure, and has m. p. 143–144° (corr.), and $[\alpha]_D^{25} + 104.9^\circ$ in chloroform. This method has also been employed in the preparation of " *β -iodoacetodextrose*," $C_{14}H_{23}O_9I$, m. p. 110–111° (corr.), $[\alpha]_D^{25} + 231.9^\circ$ in *s*-tetrachloroethane, from α - or β -penta-acetyldextrose in acetic anhydride, and hydrogen iodide in glacial acetic acid; it crystallises in colourless needles, and belongs probably to the β -series, since it is converted into tetra-acetyl- β -methyl glucoside by methyl alcohol and silver carbonate, in which case, therefore, its formation from α -penta-acetyldextrose must be accompanied by intramolecular change.

Hitherto synthetic glucosides of polyhydric alcohols have not been obtained in the crystalline state. This has now been achieved by the use of pure "bromoacetodextrose," which has the great advantage of forming easily crystallisable acetyl derivatives. *Tetra-acetyl- β -glycol-glucoside*, $C_{16}H_{24}O_{11}$, m. p. 101–103° (corr.), obtained by shaking

glycol, pure bromoacetodextrose, and dry silver carbonate for several hours, crystallises from water in stout prisms, does not reduce Fehling's solutions, has $[\alpha]_D^{25} - 26.23^\circ$ in aqueous solution, and is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding β -glycosid-*d*-glucoside, $C_2H_{10}O_7$, m. p. 137—138 (corr.). $[\alpha]_D^{18} - 30.20^\circ$ in aqueous solution, which can be obtained in stout crystals by the slow evaporation of its solution in alcohol-ethyl acetate, rapidly by inoculation when crystals have once been secured; it does not reduce Fehling's solution, and is rapidly hydrolysed by hot mineral acids and by emulsin, which indicates that the glucoside belongs to the β -series.

B. HELFERICH, by the preceding method, has obtained crystalline *d*-glucosides of benzyl alcohol, $[\alpha]_D^{20} - 55.6^\circ$, of cyclohexanol, $[\alpha]_D^{20} - 41.5^\circ$, of geraniol, $[\alpha]_D^{20} - 37.3^\circ$, of cetyl alcohol, $[\alpha]_D^{20} - 22.5^\circ$, and of glycollic acid, $[\alpha]_D^{20} - 43.8^\circ$.
C. S.

Derivatives of Cellobiose. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1910, 43, 2536—2543. Compare preceding abstract).—The experiments on cellobiose and their results are quite similar to those in the case of lactose. "*Bromoacetocellobiose*," $C_{12}H_{14}O_{10}BrAc$, is obtained by shaking octa-acetylcellobiose at the ordinary temperature with a solution of hydrogen bromide in glacial acetic acid saturated at 0° ; it crystallises in needles, darkens at 180° , and melts and decomposes a few degrees higher, and has $[\alpha]_D^{20} + 96.54^\circ$ in chloroform. "*Iodoacetocellobiose*," $C_{12}H_{14}O_{10}IAc$, prepared in a similar manner (the isomeric octa-acetyl cellobiose, m. p. 198° , may be used), forms needles, has m. p. $160-170^\circ$ (decomp.), and $[\alpha]_D^{20} + 125.6^\circ$ in chloroform and 123.2° in *s*-tetrachloroethane. From either of these compounds, by boiling with water and calcium carbonate, or by shaking with silver carbonate in a moist solvent, most conveniently in acetone, *hepta-acetylcellobiose*, $C_{12}H_{13}O_{11}Ac$, m. p. $195-197^\circ$, is obtained, which crystallises from water in slender needles, has $[\alpha]_D^{20} + 19.95^\circ$ in chloroform, 19.58° in *s*-tetrachloroethane, and 18.85° after twenty minutes and 25.48° after twenty-six hours in methyl alcohol; it dissolves easily in cold, very dilute sodium hydroxide, and is not re-precipitated by acids. When "*bromoacetocellobiose*" is shaken with dry silver carbonate in dry chloroform for a few hours, a colourless, granular powder is ultimately obtained, which is a mixture consisting chiefly of the *tetradeca-acetyl* derivative of a tetrasaccharide, $C_{24}H_{28}O_{21}Ac_{11}$; by hydrolysis in acetone with cold saturated barium hydroxide it is converted into a substance, $[\alpha]_D^{20} 18.7^\circ$ in water, which consists of a carbohydrate of high molecular weight mixed with about 30% of cellobiose, the amount of which is deduced from the reducing power of the substance and the weight of phenylcellobiosazone produced with phenylhydrazine. The carbohydrate has not been isolated in a pure state.
C. S.

Destructive Distillation of Cellulose. ERNST ERDMANN and C. SCHAEFER (*Ber.*, 1910, 43, 2398—2406).—The following substances have been obtained by subjecting cellulose to destructive distillation from a copper retort during two hours: (a) Gas containing carbon dioxide 0.2, heavy hydrocarbons 0.5, oxygen 0.9, carbon monoxide 65.5, methane 19, hydrogen 11.5, nitrogen 2.4 per cent.; (b) aqueous

liquid, about 40% of the original cellulose; this forms a reddish-brown liquid with a pungent odour, is strongly acidic, has reducing properties, and gives a deep purple coloration with ferric chloride; (c) brown mobile tar, 5% of the cellulose.

The following products have been isolated from the aqueous distillate after neutralising with sodium carbonate and subjecting to fractional distillation: Formaldehyde; furfuraldehyde; maltol (compare Brand, Abstr., 1894, i, 270; Kiliani and Balzen, Abstr., 1895, i, 80; Peratoner and Tamburello, Abstr., 1905, i, 807); ω -hydroxy-methylfurfuraldehyde, the semioxazone of which is not molten at 260°, and γ -valerolactone.

J. J. S.

Insoluble Lead Salts of Amino-acids. PHOEBUS A. LEVENE and DONALD D. VAN SLIKE (*J. Biol. Chem.*, 1910, 8, 285—286).—Both tyrosine and aspartic acid form lead salts which are nearly insoluble in water. The fact will probably be useful in the separation of these amino-acids from mixtures.

W. D. H.

Synthesis of Polypeptides. Derivatives of *L*-Leucine. EMIL ADDERHALDEN and L. E. WEBER (*Ber.*, 1910, 43, 2429—2435).—The complicated polypeptides afford materials for the study of the peptolytic enzymes. *d*-Alanyl-glycyl-glycine ($[\alpha]_D + 31^\circ$) is hydrolysed by some enzymes to *d*-alanine and inactive glycyl-glycine as shown by a decrease in rotatory power. The pressed juice of cancer cells causes an increase in rotatory power, indicating hydrolysis to glycine and *d*-alanylglycine.

In order to have further test materials available, a number of new polypeptides have been prepared containing *L*-leucine and glycine. It is found that the introduction of each glycine group causes a large increase in levorotation, an introduction of leucine working in the contrary direction.

Chloroacetyl-L-leucine, prepared by coupling the constituents in presence of sodium hydroxide, has m. p. 139—140° (corr.), $[\alpha]_D^{20} - 13.1^\circ$. By the action of ammonia at 37°, *glycyl-L-leucine* is formed, crystallising in plates which turn brown at 246° (corr.), m. p. 256° (corr., decomp.), $[\alpha]_D^{20} - 31^\circ$. From the mother liquors an insoluble compound crystallising in plates, m. p. 223° (corr.), was obtained.

d- α -Bromoisohexoyl-glycyl-L-leucine crystallises in needles, m. p. 101° (corr.), $[\alpha]_D^{20} + 30.4^\circ$.

L-Leucylglycyl-leucine, •

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{H}$, is obtained as a granular powder, m. p. 256—266° (decomp.), $[\alpha]_D^{20} + 6.0^\circ$.

Chloroacetyl-L-leucyl-glycyl-L-leucine is obtained in small, hygroscopic needles, which soften at 70°, $[\alpha]_D^{20} - 9.1^\circ$.

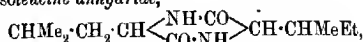
Glycyl-L-leucyl-glycyl-L-leucine is a granular powder which becomes brown at 240°, m. p. 256—257° (corr.), $[\alpha]_D^{20} - 51.0^\circ$.

L-Leucyl-glycyl-L-leucyl-glycyl-L-leucine is a crystalline powder which becomes brown at 210°, m. p. 256—266° (corr., decomp.), $[\alpha]_D^{20} - 14.5^\circ$.

E. F. A.

Synthesis of Polypeptides. Derivatives of *iso*Leucine. III.

EMIL ABDERHALDEN and PAUL HIRSCH (*Ber.*, 1910, 43, 2435—2441, Compare Abstr., 1909, i, 769).—*L*-Leucyl-*D*-isoleucine has $[\alpha]_D^{20} + 18.13^\circ$, and shows no biuret reaction.

L-Leucyl-*D*-isoleucine anhydride,

forms slender needles, m. p. 291° (corr.), $[\alpha]_D^{20} - 35.76^\circ$.

d- α -Bromopropionyl-*L*-leucyl-*D*-isoleucine, prepared by coupling the constituents in the usual manner, sinters at 153° , m. p. 164° (corr.), $[\alpha]_D^{20} - 23.37^\circ$.

d-Alanyl-*L*-leucyl-*D*-isoleucine forms minute needles, sinters at 231° , and has m. p. 245° (corr., decomp.). In *N*-hydrochloric acid it has $[\alpha]_D^{20} - 24.89^\circ$; in *N*-sodium hydroxide, $[\alpha]_D^{20} - 45.72^\circ$; in water, $[\alpha]_D^{20} - 9.12^\circ$. The tripeptide gives a violet biuret reaction and forms a copper salt.

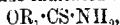
Chloroacetyl *d*-alanyl-*L*-leucyl-*D*-isoleucine separates in tiny needles, which sinter at 189° , m. p. 197° , $[\alpha]_D^{20} - 54.83^\circ$.

Glycyl-*d*-alanyl-*L*-leucyl-*D*-isoleucine, obtained by the action of ammonia on the previous compound, sinters at 231° , m. p. 251° (corr., decomp.). In *N*-hydrochloric acid, it has $[\alpha]_D^{20} - 80.59^\circ$; in *N*-sodium hydroxide, $[\alpha]_D^{20} - 73.44^\circ$. It shows a pronounced biuret coloration, and forms a copper salt. E. F. A.

Nitrogen and Sulphur Derivatives of Carbon Disulphide.

XVI. Action of Ammonia and Amines on Thiocarbonates. MARCEL DELÉPINE and PAUL SCHVING (*Bull. Soc. chim.*, 1910, [iv], 7, 894—902).—The action of ammonia and of primary and secondary amines on thiocarbonates of the following five types has been studied: $\text{SR}_1 \cdot \text{CS} \cdot \text{SR}_2$, $\text{OR}_1 \cdot \text{CS} \cdot \text{SR}_2$, $\text{OR}_1 \cdot \text{CS} \cdot \text{OR}_2$, $\text{SR}_1 \cdot \text{CO} \cdot \text{SR}_2$, $\text{OR}_1 \cdot \text{CO} \cdot \text{SR}_2$.

With ammonia at atmospheric temperatures there are formed in the course of three or four days, urethanes of the following types respectively for the compounds indicated above: $\text{SR}_1 \cdot \text{CS} \cdot \text{NH}_2$,



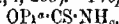
$\text{OR}_1 \cdot \text{CS} \cdot \text{NH}_2$, $\text{SR}_1 \cdot \text{CO} \cdot \text{NH}_2$, $\text{OR}_1 \cdot \text{CO} \cdot \text{NH}_2$. In the cases of types two and three some ammonium thiosulphate is formed, not as Salomon supposed (this Journ., 1873, 617), due to the presence of impurities, but to atmospheric oxidation (compare Hagemann, *Annalen*, 1882, 123, 68; 126, 297, and Conrad and Salomon, this Journ., 1875, 753). With ammonia at 100° the three first types yield ammonium thiocyanate, and types four and five, carbamide.

Primary amines react in a manner strictly analogous to ammonia, furnishing at atmospheric temperature, and in the course of several days, the corresponding urethanes, thus: $\text{SR}_1 \cdot \text{CS} \cdot \text{NHR}_3$, $\text{OR}_1 \cdot \text{CS} \cdot \text{NHR}_3$, $\text{OR}_1 \cdot \text{CS} \cdot \text{NHR}_3$, $\text{SR}_1 \cdot \text{CO} \cdot \text{NHR}_3$, $\text{OR}_1 \cdot \text{CO} \cdot \text{NHR}_3$. With excess of the primary amine at 100° the corresponding dialkylcarbamides are formed, the action taking place very slowly in the case of type two, ^{WAS} as the ester used was $\text{SMe} \cdot \text{CS} \cdot \text{OMe}$, and the amine, ethylamine, but similar results were obtained with aniline.

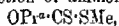
With secondary amines the action tends to remain at the urethane stage even with excess of the amine at 100—120°.

Dimethyl trithiocarbonate, $\text{CS}(\text{SMe})_2$, D_4^0 1·2820, D_4^{20} 1·2630, b p. 225°, is an orange-yellow, highly refractive oil of peculiar odour (compare Cahours, *Ann. Chim. Phys.*, 1847, [iii], 19, 158).

Ethyl diethylthiocarbamate, $\text{NEt}_2 \cdot \text{CS} \cdot \text{OEt}$, b p. 224°, is a colourless liquid. Methyl piperidylthiocarbamate, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CS} \cdot \text{OMe}$, m p. 23°, b p. 120—122°/16 mm., obtained by the action of piperidine on methyl thiothiocarbonate, $\text{OMe} \cdot \text{CS} \cdot \text{SMe}$, is crystalline, possesses a mint-like odour, evolves sulphuric acid vapours at 100°, and phosphoresces (compare this vol., i, 295). Propyl thioncarbamate,



m p. 35°, formed by the action of ammonia on the ester,

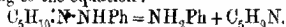


is crystalline. Methyl dimethylthiocarbamate, $\text{NMe}_2 \cdot \text{CO} \cdot \text{SMe}$, D_4^0 1·1098, D_4^{20} 1·0895, b p. 180°, obtained by the action of dimethylamine on methyl dithiocarbonate, $\text{CO}(\text{SMe})_2$, is a colourless liquid with a fungoid odour.
T. A. H.

Colour of Vanadium Thiocyanate. C. BONGIOVANNI (*Boll. chim. farm.*, 1910, 49, 467—468).—When a solution of vanadium sulphate is treated with barium thiocyanate, a green liquid is obtained, and it has consequently been supposed that vanadium thiocyanate is green, in contradistinction to the vanadithiocyanates of the alkali metals, which are violet. The author advances reasons for the view that the green colour is a result of hydrolytic processes due to the presence of sulphates. Vanadium chloride and thiocyanic acid give an intense reddish-violet coloration, which becomes green on addition of sulphates, or of ammonium oxalate or acetate. These substances also decolorise the red solution obtained when a ferric salt is treated with a thiocyanate. It appears probable, therefore, that vanadium thiocyanate has a colour similar to that of the vanadithiocyanates.

R. V. S.

New Method for the Preparation of Aliphatic Nitriles. ALEXANDER E. ARBUSOFF (*Ber.*, 1910, 43, 2296—2300).—Good yields of aliphatic nitriles can be obtained by heating the phenylhydrazones of some of the higher aliphatic aldehydes with metallic salts, such as cuprous chloride, platinumous chloride, or zinc chloride. The reaction succeeds according to the equation:



The following nitriles have been prepared by heating the phenylhydrazone with a small amount of cuprous chloride (0·2 gram) at 180—200°, and subjecting the products to fractional distillation under reduced pressure: isovaleronitrile, 56%; isobutyronitrile, 37%; heptonitrile, 60% yield.

J. J. S.

The Supposed Lead Ferricyanide is a Lead Ferricyanide-nitrate. ERICH MÜLLER and OTTO DIEFENTHÄLER (*Ber.*, 1910, 43, 2321—2323).—The dark red precipitate which is obtained by the interaction of solutions of lead nitrate and potassium ferricyanide is

not lead ferricyanide, as has hitherto been supposed, but lead ferri-cyanide-nitrate, $\text{Pb}_3[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 5\text{H}_2\text{O}$.

It is suggested that the constitution is either $\text{NO}_3 \cdot \text{Ph} \cdot \text{Pb} : \text{Fe}(\text{C}_6\text{N}_6)$ or $\text{Pb} : \text{Fe}(\text{C}_6\text{N}_6) : \text{Ph} \cdot \text{NO}_3$, and the fact that the dark red crystals give a light greenish-yellow solution indicates that there may be an equilibrium between these two forms.

T. S. P.

The Action of Hydrogen Aurichloride on Aqueous Solutions of Potassium Ferrocyanide. ERNST BEUTEL (*Monatsh.*, 1910, 31, 871—881).—The reaction between hydrogen aurichloride and potassium ferrocyanide in aqueous solution depends on the relative proportions of the two reagents. In the first experiments a solution containing 4.6400 grams of hydrogen aurichloride and 8.5356 grams of potassium ferrocyanide per litre was used, this corresponding with 4 mols. of the former to 3 mols. of the latter compound. The solution, when made, rapidly became emerald-green, changing to deep blue in the course of twelve hours. At the end of eight days, during which the solution was exposed to sunlight in a sealed flask, a deep blue precipitate had deposited, leaving a colourless, supernatant liquid. The precipitate consisted of pure ferric ferrocyanide, and the supernatant liquid contained the aurocyanide, auricyanide, and aurichlorocyanide of potassium, potassium chloride, and hydrochloric acid. The quantitative results were in accordance with the equation: $28\text{HAuCl}_4 + 21\text{K}_4\text{FeC}_6\text{N}_6 = 8\text{KAuCl}_2\text{N}_4 + 6\text{KAuCl}_2\text{N}_2 + 14\text{KAuCl}_2\text{C}_2\text{N}_2 + 56\text{KCl} + 28\text{HCl} + 3\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$. The reaction products could not, for the most part, be isolated from the solution, owing to the fact that on concentration the complex cyanides are decomposed by the hydrochloric acid with the formation of aurous cyanide. Potassium auricyanide was isolated, since it resists the action of the mineral acid to a great extent.

The supernatant liquid already mentioned will enter into further reaction with the two reagents. With hydrogen aurichloride, it turns sulphur-yellow, and aurous cyanide is precipitated after a short time. With potassium ferrocyanide, it turns green, and then gives a bluish-green precipitate of a mixture of ferric hydroxide and ferric ferrocyanide. On long exposure to the light, the precipitate becomes pure ferric hydroxide only. Exact equations could not be given for these reactions.

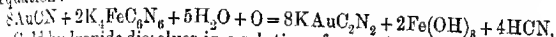
In the next series of experiments, approximately equimolecular solutions of the two reagents (10 grams of hydrogen aurichloride per litre = A ; 10 grams of potassium ferrocyanide per litre = B) were mixed in varying proportions. With mixtures varying from $3A:B$ to $25A:B$, the chief reaction is the precipitation of aurous cyanide. With $A:B$, the solution gradually changes from a light green to a dark brown, and retains the latter colour for a long time in diffused daylight or in the dark, no precipitate being formed. On exposure to sunlight, the colour changes to emerald-green, then dark blue, and finally disappears, a dark blue precipitate being deposited. With $A:2B$ an emerald-green solution is obtained immediately, and the solution gradually, quicker on warming, deposits blue ferric ferrocyanide, leaving a yellow supernatant liquid containing the excess of potassium ferrocyanide. Similar results are obtained with $A:3B$ and

$A:5B$, but the blue precipitate takes much longer to form. With $A:10B$ and $A:25B$, green solutions are obtained, which only on long keeping in sunlight deposit small quantities of ferric hydroxide, leaving a yellow solution containing ferro- and ferri-cyanide.

Potassium ferricyanide behaves similarly to potassium ferrocyanide towards hydrogen auric chloride, but a quantitative investigation is still wanting.

T. S. P.

Action of Aqueous Solutions of Potassium Ferrocyanide on Aurous Cyanide and Gold Hydroxide. ERNST BEUTEL (*Monatsh.*, 1910, 31, 883—886).—When aurous cyanide is heated with a solution of potassium ferrocyanide, oxygen being passed through the solution during the heating, it dissolves with the formation of potassium aurocyanide, ferric hydroxide being precipitated according to the equation:

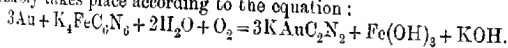


Gold hydroxide dissolves in a solution of potassium ferrocyanide with the formation of potassium gold cyanide and the precipitation of ferric hydroxide. The reaction takes place at room temperature, but much quicker on warming. Quantitative experiments were not made, and the particular potassium gold cyanide formed is not stated.

Fulminating gold also dissolves in solutions of potassium ferrocyanide. The solution first becomes emerald-green, and hydrogen cyanide is evolved. A green precipitate is then produced, which finally changes to brown ferric hydroxide. Potassium gold cyanide remains in solution.

T. S. P.

Solubility of Finely-divided Gold in Solutions of Potassium Ferrocyanide. ERNST BEUTEL (*Monatsh.*, 1910, 31, 887—890).—Finely-divided gold will dissolve completely in solutions of potassium ferrocyanide at room temperature. The rate of solution is very slow, even at the boiling point. Potassium aurocyanide is formed, and the resulting ferro-ions are oxidised by the oxygen of the air, giving ferric hydroxide. The solution formed is alkaline. The reaction probably takes place according to the equation:



T. S. P.

Estimation of Diazo-alkyls. E. K. MARSHALL and SALOMON F. ACKEE (*Ber.*, 1910, 43, 2323—2330).—Wegscheider and Gehring's statement (*Abstr.*, 1903, i, 685), that the yield of ester obtained by the action of an ethereal solution of diazomethane on an acid is greater than would be expected from the concentration of the diazomethane solution as determined by titration with iodine (Pechmann, *Abstr.*, 1894, i, 438), is confirmed. The same solution of diazomethane does not give concordant results when titrated by the iodine method.

For estimating the concentration of a diazomethane solution, the authors recommend the use of an excess of *m*- or *p*-nitrobenzoic acid in ethereal solution and titrating the excess of acid by means of standard alkali after diluting with water, or actually isolating the ethyl ester by extraction with chloroform after shaking with water.

and sodium hydrogen carbonate solution. The results are correct to within 2—3%. Low results are obtained in the presence of alcohol.

Diazoethane can be estimated in a similar manner.

J. J. S.

The Alkyl and Aryl Compounds of Tin. PAUL PFEIFFER [with R. LEHNHARDT, H. LEFTENSTEINER, RUDOLF PRADÉ, K. SCHNEERMANN, and P. TRUSKIER] (*Zeitsch. anorg. Chem.*, 1910, 68, 102—122).—A number of organic derivatives of quadrivalent tin have been described, as a preliminary to the study of their molecular compounds for comparison with those of cobalt, chromium, and platinum.

In the preparation of methylstannic acid from methyl iodide and an aqueous-alcoholic solution of potassium stannate, carbon dioxide precipitates small, glistening crystals of *potassium methylstannicarbonate*, $\text{SnMeO} \cdot \text{O} \cdot \text{CO}_2\text{K} \cdot \text{H}_2\text{O}$, an aqueous solution of which decomposes on boiling, yielding methylstannic acid.

Dimethylstannic halides are best prepared by heating tin with methyl iodide, converting the product into oxide by means of ammonia, and then into the chloride by means of hydrogen chloride. After crystallising from light petroleum to remove the monomethyl compound, the chloride is converted into the oxide and then into the required salts. The chloride, bromide, and iodide have m. p.'s 108° , 78° , and 43° respectively. *Dimethylstannic oxalate*, $\text{SnMe}_2\text{C}_2\text{O}_4$, forms a white precipitate, soluble in a solution of potassium oxalate. *Dimethylstannic sulphide* is a white precipitate, soluble in ammonium sulphide.

Dipropylstannic bromide, SnPr_2Br_2 , forms large, colourless needles, m. p. 49° .

Dibutylstannic oxide, $\text{SnO}(\text{C}_4\text{H}_9)_2$, when prepared by the action of aqueous-alcoholic ammonia on the pure chloride, forms an insoluble, amorphous powder. The *chloride*, $\text{Sn}(\text{C}_4\text{H}_9)_2\text{Cl}_2$, is sparingly soluble in water and has m. p. 43° ; the *bromide* has m. p. 20° .

Diisobutylstannic oxide yields a basic chloride, m. p. 145° , on treatment with hydrochloric acid followed by pyridine.

Tribenzylstannic chloride, $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$ (Abstr., 1904, i, 232), melts at 142 — 144° after crystallisation from glacial acetic acid. Pyridine is without action on it. Sodium carbonate solution converts it into *tribenzylstannic hydroxide*, $\text{Sn}(\text{C}_6\text{H}_5)_3\text{OH}$, crystallising in colourless, rhombic tablets, m. p. 117 — 121° . It is insoluble in water, but soluble in many organic solvents. Acetyl or benzoyl chloride converts it into the chloride, and not into the acetate or benzoate, in this respect resembling the reaction with the corresponding silicon compounds (Robison and Kipping, Trans., 1908, 93, 439). *Tribenzylstannic bromide* has m. p. 125 — 128° .

Tin tetrapropyl boils at 228° .

Tin tetra-p-tolyl, $\text{Sn}(\text{C}_6\text{H}_4\text{Me})_4$, prepared by the action of magnesium, followed by stannic bromide, on *p*-bromotoluene, forms colourless, glistening needles, m. p. 230° .

C. H. D.

Constituents of Coal Tar. VI. *iso*Propylbenzene (Cumene). GUSTAV SCHULTZ (*Ber.*, 1910, 43, 2517—2521. Compare this vol., i, 897).—[With A. SZÉKELY].—The viscous, brown, crude acids

obtained by the sulphonation of the "mesitylene" fraction are decomposed by superheated steam, and the resulting hydrocarbons are repeatedly distilled, whereby a fraction, b. p. 150—161°, is obtained, from which cumene is isolated as follows. The fraction is nitrated, and the portion of the product which is easily volatile with steam is fractionally distilled; the chief portion, b. p. 145—150°/30—32 mm., is redistilled, whereby a *nitro*-compound, $C_9H_{11}O_2N$, b. p. 240—245° or 130—133°/15—16 mm., is obtained, which is proved to contain nitro-cumene by the following experiments. A portion is reduced by tin and hydrochloric acid, and the amino, b. p. 223—230°, is separated into three fractions, b. p. 223—225°, 225—228°, and 228—230°. The first fraction is treated with the calculated quantity of oxalic acid, whereby the oxalates of *p*-cumidine and of *o*-cumidine are obtained; also a portion of the fraction, after being acetylated, yields aceto-*p*-cumidine and acetomesidine. Another portion of the nitro-compound is boiled with 3 parts of nitric acid, D 1.48, and 4.5 parts of water for six days, whereby *p*-nitrobenzoic acid is produced. A third portion yields by further nitration trinitromesitylene and other trinitro-compounds which have not been separated.

A portion, b. p. 150—155°, of the original oil is sulphonated by concentrated and fuming sulphuric acids, and from the products *o*-isopropylbenzenesulphonic acid has been isolated in the form of the sulphonamide, m. p. 96—98°.

C. S.

3:3-Dimethyldiphenyleneiodonium Hydroxide and Some of Its Salts. LUIGI MASCARELLI and T. CERASOLI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 308—311. Compare Abstr., 1909, i, 907).—3:3-Dimethyldiphenyleneiodonium iodide is obtained in small quantity by diazotising 6:6'-diamino-3:3'-dimethyldiphenyl and treating the product with potassium iodide. It yields the above *hydroxide* when treated with moist silver oxide. The *iodide* is a yellow powder, m. p. 246°. The *bromide* is a white powder becoming yellow, m. p. 281°. The *chloride* forms a white, microcrystalline powder, becoming brown, m. p. 290°. The *oxalate*, $(\begin{smallmatrix} C_6H_3Me \\ C_6H_3Me \end{smallmatrix} > I)_2C_2O_4$, forms colourless, acicular crystals, m. p. 228°.

R. V. S.

Esters of Benzenesulphon-nitroanilides. STANISLAUS OPOLSKI (*Bull. Acad. Sci. Cracow*, 1910, 126—128. Compare Abstr., 1907, i, 908).—To complete the proof that intramolecular change occurs when the three almost colourless benzenesulphon-nitroanilides are converted into their highly coloured salts, it is necessary to isolate the coloured *aci*-esters in addition to the ordinary colourless esters. All attempts to isolate the former, however, have been unsuccessful. By the action of alkyl iodides on the silver salts, the colourless esters are obtained, together with a red oil, from which a crystalline substance cannot be isolated.

The trinitro-compound obtained by the nitration of benzenesulphon-nitroanilide or of benzenesulphon-*p*-nitroanilide must be benzene-

sulphonpicramide, but attempts to prepare it by the condensation of picramide and benzenesulphonyl chloride, or of picryl chloride and benzenesulphonamide, have been unsuccessful.

Benzenesulphon-o-nitroethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt} \cdot \text{SO}_2\text{Ph}$, m. p. 103—104°, and *benzenesulphonbenzyl-o-nitroanilide*,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_2\text{Ph}) \cdot \text{SO}_2\text{Ph}$, m. p. 148—149°, unlike the colourless methyl esters, have a distinct yellow tinge. *Benzenesulphonmethylpicramide*,

$(\text{NO}_2)_3 \cdot \text{C}_6\text{H}_2 \cdot \text{NMe} \cdot \text{SO}_2\text{Ph}$, m. p. 181—182°, forms colourless crystals. C. S.

Preparation of Aromatic Alkyl Ethers. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224388).—An extension of the work described in the chief patent (Abstr., 1908, i, 263) to the reaction between substances containing one or more phenolic hydroxyl groups and the nitroso-compounds of acid amides of the general formula $\text{-NR} \cdot \text{NO}$, where $\text{R} = \text{alkyl}$.

The product obtained from β -naphthol and nitrosobenzenesulphonethylamide has m. p. 60°. When morphine suspended in methyl alcohol is treated with *p*-toluenesulphononitrosomethylamide in the presence of an alkaline hydroxide, a crystalline compound, m. p. 60°, is obtained.

Nitroso- β -naphthalenesulphonmethylamide has m. p. 85°. The morphine and β -naphthol in the foregoing condensations can be replaced by other phenols, cresols, or dihydroxybenzenes. F. M. C. M.

Acenaphthene. FRANZ SACHS and GERHARDT MOSEBACH (*Ber.*, 1910, 43, 2473—2475).—4-Aminoacenaphthene yields the 4-halogen derivatives of acenaphthene when treated according to the Sandmeyer reaction. An intense dark green coloration is produced on diazotisation. 4-Chloroacenaphthene forms slender needles, m. p. 62·5—63°; 4-bromoacenaphthene has m. p. 51·5° (compare Graebe, Abstr., 1903, i, 408); 4-iodoacenaphthene crystallises in rosettes of colourless, slender needles, m. p. 63—63·5° [compare Crompton, Proc. 1910, 26, 226]. E. F. A.

Structure of Pyrene. EGON LANCSTEIN (*Monatsh.*, 1910, 31, 861—870. Compare Goldschmidt, Abstr., 1907, i, 310).—The formulae for pyrene and pyrenic acid deduced by Goldschmidt are confirmed by isolation of two isomeric methyl hydrogen pyrenates,



The α -ester, prepared by heating the anhydride with a large excess of pure methyl alcohol, crystallises in large needles of a golden-yellow colour and yields golden-yellow solutions. The β -ester crystallises in yellowish-green, slender needles, usually arranged in nodules; its solutions are brownish-green, and it is twice as soluble in alcohol as the α -ester. When heated, the β -ester turns brown more rapidly than the α -ester, and decomposes more quickly.

peri-Trimethylenenaphthalic anhydride (formula I) is obtained when pyrenic acid is reduced by boiling with hydriodic acid (D. 146)

and red phosphorus. It crystallises from alcohol in colourless, glistening needles, decomposing at about 260° . Its solution in concentrated sulphuric acid has a deep blue fluorescence, and its alcoholic solution a green fluorescence. The corresponding acid, $C_{15}H_{12}O_4$, is colourless, and does not readily yield crystalline salts. When the barium salt is heated with lime, *peri-trimethylenenaphthalene*,



$C_{15}H_{12}$, is obtained, and this crystallises from dilute alcohol in colourless, glistening plates, m. $68-69^{\circ}$. It turns yellow on exposure to the air, and yields a *picrate* in the form of glistening, red needles, m. p. 127° after turning brown at 80° . The formation of this picrate is used as an argument in favour of the constitutional formula ascribed to the hydrocarbon, as hydronaphthalenes do not yield picrates.

Hexahydropyrene (Goldschmiedt, *loc. cit.*) has m. p. $129-130^{\circ}$, and in the presence of excess of picric acid yields a red *picrate*, m. p. 119° . The constitution ascribed to the hexahydro-compound is therefore that of a *diperiditrimethylenenaphthalene*. J. J. S.

Reduction of Nitrobenzene to Aniline. C. NICOLESCU OTIN (*Zeitsch. Elektrochem.*, 1910, 16, 674-680).—The author has tried most of the methods which have been proposed for reducing nitrobenzene to aniline by electrolysis. His results are tabulated, and show that the yields of aniline are usually poor (from 19 to 88%); considerable quantities of other materials are consumed in many of the processes, and undesirable by-products are often formed. He shows that the conditions necessary for a good yield are a very large cathode surface and a considerable excess of hydrochloric acid.

Using 120 c.c. of hydrochloric acid (D 1.19) to 20 grams of nitrobenzene and a cathode consisting of lead wool, or nickel wire in sufficient quantity to fill the whole cathode compartment (the anode is a lead cylinder immersed in sulphuric acid contained in a porous pot), he obtains 92 to 94% of the theoretical quantity of aniline with a current efficiency of 94 to 97%. T. E.

[Chromoisomeric and Homochromoisomeric Nitroanilines.] ARTHUR HARTZSCH (*Ber.*, 1910, 43, 2516. Compare this vol., i, 475).—The following corrections are made. Priority is given to Flürscheim in the preparation of *s*-nitrophenylenediamine. *o*-Tolyl-2:4-dinitroaniline darkens at 120° , and has m. p. $128-129^{\circ}$. Also, a reply is given to Busch (this vol., i, 617) on the isomerism of the two *peryl*-methylanilines. C. S.

[Preparation of Derivatives of *p*-Toluenesulphon-*p*-nitroanilide.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 224499).—*p*-Toluenesulphon-*p*-nitroanilide when treated with methyl chloride yielded *p*-toluenesulphonmethyl-*p*-nitroanilide, m. p. $175-176^{\circ}$; this on reduction with sodium sulphide was converted into *p*-toluenesulphonylmethyl-*p*-phenylenediamine, m. p. 135° , a grey powder some-

what readily soluble in alcohol, more sparingly so in benzene. This base was diazotised and combined in alkaline solution with 8-acetyl-amino-1-naphthol-3:6-disulphonic acid (or similar acids), and the separated product treated during several hours with sulphuric acid at a temperature of 15—20°, whereby the toluenesulphonyl group only was eliminated; the final products were violet-blue dyes, very stable to alkalis and light.

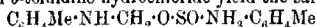
F. M. G. M.

Hypo-sulphites. VII. Rongalite and Salts of Amines. ARTHUR BINZ and TH. MARX (*Ber.*, 1910, 43, 2344—2349. Compare Binz and Isaac, *Abstr.*, 1908, i, 940).—The hydrochlorides of amines react with rongalite even in the absence of formaldehyde. It is suggested that the hydrochloride first condenses with the sodium salt according to the equation

$\text{RNH}_2\cdot\text{HCl} + \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{S}\cdot\text{ONa} = \text{RNH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{S}\cdot\text{OH} + \text{NaCl} + \text{H}_2\text{O}$, and that the substituted formaldehydesulphoxylic acid then forms a salt with the excess of the amine hydrochloride:

$\text{RNH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{S}\cdot\text{OH} + \text{RNH}_2\cdot\text{HCl} = \text{RNH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{S}\cdot\text{O}\cdot\text{NH}_2\text{R} + \text{HCl}$, and that it is this salt which is precipitated. In the case of ammonium chloride and of hydroxylamine hydrochloride, it has been found possible to isolate the intermediate product. The salts are decomposed by cold dilute sodium hydroxide solution, and practically half the amine used up in the formation of the compound is liberated.

Rongalite and *o*-toluidine hydrochloride yield the salt



in the form of colourless crystals, m. p. 101—104°. It turns a yellow colour on exposure to the air, and reduces warm indigocarmin solution. When an excess of rongalite is used, mixtures are formed.

Rongalite and anthranilic acid hydrochloride yield colourless crystals of the compound $\text{C}_{15}\text{H}_{16}\text{O}_6\text{N}_2\text{S}$, m. p. 143° (decomp.). When diazotised, it yields salicylic acid, and when oxidised with hydrogen peroxide or with sodium thiosulphate yields anthranilic acid. Rongalite and hydroxylamine hydrochloride in the presence of formaldehyde solution yield *hydroxylaminomethylsulphurous acid*, $\text{OH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{H}$, owing to the oxidising action of the hydroxylamine. It can be crystallised from water, does not reduce indigocarmin, and has m. p. 191°.

J. J. S.

Preparation of Thiodiphenylamine and its Derivatives. FRITZ ACKERMANN (D.R.-P. 224348).—The preparation of thiodiphenylamines with the aid of sulphur and aluminium chloride has previously been described; it is now found that aluminium bromide or iodide, ferric chloride, antimony trichloride, cuprous iodide, sulphur iodide, or iodine can be employed equally well, and the methods of doing so with their extension to the preparation of thio- β -dinaphthylamine and thio-phenyl- β -naphthylamine are described. *Thio-p-tolyl- β -naphthylamine* was obtained as a greenish-yellow powder, m. p. 182°. F. M. G. M.

Action of Magnesium Alkyl Halides on Anilides and their Chlorides. MAX BUSCH and MARTIN FLEISCHMANN (*Ber.*, 1910, 43, 2553—2556).—Beis has shown that the interaction of acid amides

and magnesium alkyl halides leads to the formation of ketones and ammonia (Abstr., 1904, i, 15). When the aminic hydrogen atoms are replaced by alkyl groups, the authors find that a dual reaction occurs; thus, magnesium phenyl bromide (2 mols.) and benzoyl ethylaniline in ether yield ultimately benzophenone and ethylaniline (from $\text{OMgBr} \cdot \text{CPh}_2 \cdot \text{NEtPh}$), and also triphenylmethyl ethylaniline, $\text{CPh}_3 \cdot \text{NEtPh}$,

m. p. 92° (from $\text{OMgBr} \cdot \text{CPh}_3 \cdot \text{NEtPh}$ and PhMgBr), which easily decomposes in alcoholic solution into triphenylcarbinol and ethylaniline.

Magnesium alkyl halides react with imino-chlorides generally either at the double linking or at the reactive halogen atom, yielding the same product in both cases, but sometimes at both of these points of attack. Thus benzanilideimino-chloride and ethereal magnesium methyl iodide yield ultimately acetophenoneanil, $\text{NPh} \cdot \text{CPhMe}$, which cannot be isolated, but the presence of which is proved by hydrolysis with hydrochloric acid, whereby acetophenone and aniline are obtained. In a similar way the imino-chloride reacts with magnesium ethyl bromide to form ultimately an anil which yields aniline and phenyl ethyl ketone by hydrolysis, and with magnesium phenyl bromide to form ultimately benzophenoneanil, m. p. $113-114^\circ$; once in the latter preparation a considerable amount of triphenylmethyl aniline, $\text{CPh}_3 \cdot \text{NHPh}$, was obtained, but the conditions of its formation could not be repeated.

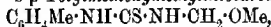
C. S.

Metathetical Reactions: Ether-thiocarbamides and their Relation to ψ -Ammonium Bases. TREAT B. JOHNSON and HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1910, 32, 1279-1285).—Cyclic quaternary bases (pyridines, quinolines, isoquinolines, and acridines) undergo isomeric change in aqueous solution, the hydroxyl group of the base migrating from the nitrogen to a carbon atom with formation of ψ -ammonium bases. The latter compounds react with alcohols at the ordinary temperature with loss of a molecule of water and production of alcoholates or ethers. When these alcoholates are warmed with alcohols, the alkyl group of the alcoholate is replaced by that of the alcohol. The mechanism of this change has been interpreted in different ways (compare Decker, Abstr., 1900, i, 522, and Gadamer, Abstr., 1905, i, 368; 1908, i, 322). In order to throw further light on these transformations, a study has been made of some ether-thiocarbamides.

The ether-thiocarbamides, $\text{OR} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHR}'$, were obtained by the action of certain thiocarbimidomethyl ethers, $\text{RO} \cdot \text{CH}_2 \cdot \text{NCS}$, on organic bases (Johnson and Guest, Abstr., 1909, i, 371). These substances are closely related to the cyclic alcoholates, as they contain the same complex, $\text{C} \cdot \text{N} \cdot \text{CH} \cdot \text{OR}$, and hence may be regarded as acyclic ψ -ammonium compounds. The ether-thiocarbamides would therefore be expected to undergo transformations with alcohols analogous to those which take place with the cyclic alcoholates, and such has been found to be the case. All the ether-thiocarbamides which have been examined react with alcohols on warming, with transposition of the alkyl groups. These reactions are reversible, and are not affected by

the b. p.'s of the alcohols or by the size of the alkyl groups involved. It is therefore possible to obtain a whole series of ether-thiocarbamides from one thiocarbimidomethyl ether. These transformations are most easily explained by assuming that unstable additive compounds are first formed, and that these decomposes with production of a new thiocarbamide and alcohol.

s-Phenylmethoxymethylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OMe}$, m. p. 133°, obtained by recrystallising *s*-phenylethoxymethylthiocarbamide or *s*-phenylisocamylloxymethylthiocarbamide from methyl alcohol, forms prismatic crystals. *s*-p-Tolylmethoxymethylthiocarbamide,



m. p. 129°, is obtained by the action of methyl alcohol on the corresponding ethoxy-compound.

E. G.

Replacement of Halogen by the Nitro-group. II. L. CHAS. RAIFORD and FREDERICK W. HEYL (*Amer. Chem. J.*, 1910, 44, 209—219).—It has been found previously (this vol., i, 373) that when 2:4:6-tribromophenol is treated with nitrous acid, a mixture of 4:6-dibromo-2-nitrophenol and 2:6-dibromo-4-nitrophenol is produced, but that 2:4:6-trichlorophenol is not affected by nitrous acid. In view of these results, it was considered of interest to study the behaviour of 2:4:6-tri-iodophenol. The work has also been extended to 2:4:6-tribromoresorcinol.

2:4:6-Tri-iodophenol has m. p. 158°, instead of 156°, as stated by Messinger and Vortmann (*Ahstr.*, 1889, 1150). The *acetate*, m. p. 154°, forms colourless needles. When sodium nitrite is added gradually to a solution of 2:4:6-tri-iodophenol in a mixture of glacial acetic acid and benzene at 12—15°, 4:6-di-iodo-2-nitrophenol is obtained, together with 2:6-di-iodo-4-nitrophenol, m. p. 155°, which forms nearly colourless prisms. It is probable that a small quantity of an iododinitrophenol is also produced in this reaction. On reducing 4:6-di-iodo-2-nitrophenol with stannous chloride in presence of hydrochloric acid, the *hydrochloride* of 4:6-di-iodo-2-aminophenol is obtained, which crystallises in long prisms.

When a solution of 2:4:6-tribromoresorcinol in glacial acetic acid is treated with sodium nitrite at 12—15°, 2:6-dibromo-4-nitroresorcinol, m. p. 143°, is produced, which forms maroon prisms or orange needles; its *ammonium* salt crystallises in deep yellow prisms. On reducing this nitro-compound with a solution of stannous chloride in hydrochloric acid, the *hydrochloride* of 2:6-dibromo-4-aminoresorcinol is obtained. 2:6-Dibromo-4-aminoresorcinol darkens above 135°, and decomposes above 175° without melting; it crystallises in prisms which are at first colourless, but soon become grey; the *picrate* begins to decompose at 220° without melting. 2:6-Dibromo-4-acetylaminoresorcinyl *diacetate*, m. p. 174—175°, forms colourless, hexagonal plates.

E. G.

Preparation of *o*- and *p*-Nitrophenols. R. S. HART (*J. Amer. Chem. Soc.*, 1910, 32, 1105—1106).—Phenol (50 grams) dissolved in alcohol (5 grams) is added drop by drop (30 drops a minute) to a solution of sodium nitrate (80 grams) in sulphuric acid (100 grams) diluted with 200 c.c. of water at 25°. The mixture is stirred vigorously

during the addition, and for half an hour afterwards. After an hour and a-half, the liquid is treated in the usual way, and gives a yield of 30 grams of *o*-nitrophenol and 13 grams of *p*-nitrophenol. W. O. W.

Phenyl Ether and Some of its Derivatives. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1910, 32, 1285—1294).—The ethers used in this investigation were prepared by distilling the aluminium derivatives of the corresponding phenols. Good yields were obtained of phenyl and *m*-tolyl ethers, but only small yields of *o*- and *p*-tolyl ethers. On rapidly distilling aluminium *p*-tolyl oxide, flashes appeared on the surface of the liquid. When some aluminium *p*-tolyl oxide which had been exposed to the air for about two months was distilled, *p*-cresol was obtained, but very little *p*-tolyl ether. The causes of these phenomena are being investigated.

Tetrabromophenyl ether, $\text{O}(\text{C}_6\text{H}_3\text{Br}_2)_2$, h. p. 280—290°/25 mm., 410—425°/760 mm., m. p. 83—84°, prepared by slowly adding an excess of bromine to a solution of phenyl ether in carbon disulphide containing a little iodine to serve as a carrier, forms large needles. It was not found possible to obtain a more highly brominated derivative.

*Dibromo-*m*-tolyl ether*, $\text{O}(\text{C}_6\text{H}_3\text{MeBr})_2$, h. p. about 250°/15 mm. and 340—350° (uncorr.)/760 mm., m. p. 43°, prepared by slowly adding the calculated quantity of bromine to a solution of *m*-tolyl ether in carbon disulphide, forms white crystals. *Tetrabromo-*m*-tolyl ether*, $\text{O}(\text{C}_6\text{H}_3\text{MeBr}_2)_2$, h. p. 260—270°/35 mm., is obtained by the action of an excess of bromine on *m*-tolyl ether in presence of a little iodine as a viscous substance which slowly crystallises. A more highly brominated derivative could not be obtained.

*2:4-Dinitrophenyl *p*-tolyl ether*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, m. p. 93°, prepared by the action of potassium *p*-tolyl oxide on 1-bromo-2:4-dinitrobenzene, forms yellow crystals. The *sulphonic acid*,

$\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, m. p. 150° (decomp.), crystallises in slender needles containing $1\frac{1}{2}\text{H}_2\text{O}$; its *barium* and *sodium* salts are described. When a solution of 2:4-dinitrophenyl *p*-tolyl ether in glacial acetic acid is warmed with chromic anhydride, it is converted into *p*-2:4-dinitrophenoxycarboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, a yellow substance which does not melt below 200°; its *silver* salt is described.

2:4-Dinitrophenyl ether, $\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, m. p. 70°, h. p. 230—250°/27 mm., obtained by the action of potassium phenoxide on 1-bromo-2:4-dinitrobenzene, is a crystalline substance with a faint odour and a pungent taste. The *sulphonic acid*, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, forms white, pearly flakes; its *barium* salt is described. *Trinitrophenyl ether*, $\text{C}_6\text{H}_2\text{O}(\text{NO}_2)_3$, prepared by dissolving 2:4-dinitrophenyl ether in concentrated nitric acid, crystallises in clusters of yellow prisms.

A bibliography of phenyl ether and its derivatives is appended.

E. G.

Organic Compounds of Quadrivalent Tellurium. CHARLES LEDERER (*Compt. rend.*, 1910, 151, 611—612).—Tellurium tetrachloride (1 mol.) reacts with magnesium phenyl bromide (5 mols.) in

dry ether. In addition to chlorobenzene, diphenyl, and diphenyl telluride, the product yields a sparingly soluble material when treated with a limited amount of water. On treatment with aqueous potassium iodide this furnishes *diphenyltellurium diiodide*, decomposing at 236—237°, and *triphenyltelluronium iodide*, TePh_3I . The latter crystallises in colourless needles, m. p. 247—248°, and on treatment with silver chloride or bromide gives the corresponding *chloride*, m. p. 244—245° (decomp.), and *bromide*, m. p. 259—260°.

Fixation of hydrogen chloride by diphenyltellurium leads to the formation of the *compound*, TeHPh_2Cl , m. p. 233—234°. W. O. W.

Preparation of Neutral Phenolic Esters of Diglycollic Acid. C. F. BOEHRINGER & SÖHNE (D.R.-P. 223305).—The phenyl esters of diglycollic acid are readily prepared by treating the acid dichloride with the required phenol or sodium phenoxide (substituted or otherwise) in the presence of an indifferent base, such as dimethylaniline.

Diphenyl diglycollate, $\text{O}(\text{CH}_2\cdot\text{CO}_2\text{Ph})_2$, forms colourless needles, m. p. 80°.

Disalicyl diglycollate forms colourless crystals, m. p. 173°; the α -*naphthyl* ester, colourless leaflets, m. p. 136°; the β -*naphthyl* ester, a colourless, crystalline powder, m. p. 160°; the *guaiacol* ester, colourless needles, m. p. 82°; the *o*-*tolyl* ester, needles, m. p. 101°; the *m*-*tolyl* ester, needles, m. p. 63°; the *p*-*tolyl* ester, needles, m. p. 89°; the *o*-*chlorophenyl* ester, needles, m. p. 129°; the *p*-*chlorophenyl* ester, slender needles, m. p. 130°; the *o*-*nitrophenyl* ester, colourless leaflets, m. p. 164°, and the *p*-*nitrophenyl* ester, a colourless, crystalline powder, m. p. 131°.

The solubility of these compounds in numerous solvents is fully described in the patent. F. M. G. M.

[Simple Formation of Benzyl Ethers.] JULIUS VON BRAUN (*Ber.*, 1910, 43, 2594).—Reply to Halban (this vol., i, 619). C. S.

The Addition of Bromine to Unsaturated Compounds. I. Allyl and Propenyl Derivatives of Benzene. GINO ARATI (*Gazzetta*, 1910, 40, ii, 89—94. Compare Abstr., 1909, i, 104).—A comparison of the velocity of addition of bromine in chloroform solution to chavicol and anethole, eugenol and *isoeugenol* and their methyl derivatives, safrole and *isosafrole*, myristicin and *isomyristicin*, and apiole and *isopiole*, show that the velocity is always greater in the case of the propenyl derivative.

The molecular refractive indices of myristicin and *isomyristicin* have also been measured, and are found to be M_d 89.44 and M_d 92.94 respectively. C. H. D.

The Xylenol from Dehydracetic Acid. EMILIO CARLINPANTI and A. GERMAIN (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 234—236).—The xynol produced when dehydracetic acid is distilled with calcium oxide is not *o*-4-xylenol, as stated by Tivoli (Abstr., 1891, 1455), but the 1:3:5-compound. The mistake is due to the fact that a substance is also formed which gives a reaction

with ferric chloride similar to that of *o*-4-xyleneol, and this impurity can only be removed by repeated crystallisation. When calcium acetate is heated with calcium oxide, a yellow oil, b. p. 215–225°, is obtained, which has no phenolic properties, but gives an intense coloration with ferric chloride. To explain the formation of *m*-5-xyleneol, the following mechanism is suggested. Dehydracetic acid under the conditions of the experiment yields acetyltriacetic acid, which loses carbon dioxide and is converted into diacetylacetone, which decomposes into acetic acid and acetylacetone; this then condenses with the acetone formed from the calcium acetate. In confirmation of this view, the authors find that *m*-5-xyleneol is produced when a mixture of the vapours of these two substances is led over calcium oxide at 400°.

5-Hydroxy-*m*-xyl phenylcarbamate. $C_8H_9O \cdot CO \cdot NHPh$, crystallises in shining needles, m. p. 148–149°. R. V. S.

Fluorenyl Ethers. ALFRED KLIEGEL (*Ber.*, 1910, 43, 2488–2496. Compare Abstr., 1905, i, 187).—Schmidt and Stützel (this vol., i, 29) on reducing fluorenoneoxime by tin and hot concentrated hydrochloric acid obtained fluoronyl ether, possessing a red colour, and quite different from the fluorenyl ether obtained by Barbier from fluorenyl alcohol. This red compound, the colour of which was attributed to the accumulation of benzene nuclei, is not in agreement with Witt's theory of colour.

By the action of silver oxide on 9-chlorofluorene, fluorenyl ether was obtained in colourless, lustrous plates, m. p. 238°, and it is further shown that the red compound of Schmidt and Stützel is in reality diphenylene-phenanthrene, m. p. 257°, coloured red by admixture with di-biphenylene ethylene, m. p. 187°.

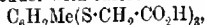
The first product of the action of hydrochloric acid and tin, or, better, of stannous chloride, is a glistening, red, crystalline compound, which is a stannichloride of 9-iminofluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:NH$. The picrate crystallises in lustrous, orange needles, and when decomposed with ammonia yields the crystalline base, which separates in pale straw-yellow, slender needles, m. p. 124°. On warming with water, it readily decomposes into ammonia and ketone. An egg-yellow and an orange oxalate and a similarly coloured sulphate were also isolated. The acetate crystallises in citron-yellow needles, m. p. 104°. E. F. A.

[*m*-Hydroxyphenyl Mercaptan.]. LADISLAUS VON SZATHMÁRY (*Ber.*, 1910, 43, 2485–2487).—Sodium *m*-benzenedisulphonate was converted into sodium *m*-phenolsulphonate, and this into the sulphonyl chloride, which was obtained as a viscid, oily, brown product having a pungent, disagreeable odour. It is reduced by tin and hydrochloric acid to *m*-hydroxyphenyl mercaptan. This crystallises when strongly cooled, but is oily at the ordinary temperature. It has a pungent, unpleasant odour, and with lead acetate yields an insoluble, stable, yellow precipitate of the lead salt, $Pb(S \cdot C_6H_4 \cdot OH)_2$. It shows no coloration with either sulphuric acid or sodium hydroxide. E. F. A.

Symmetrical Trithiophenols. JACQUES POLLAK and R. TUCKAHOVIĆ (*Monatsh.*, 1910, 31, 695—707).—*Trithiomethylphloroglucinol* [*toluene*: 2:4:6-*trithiol*], $C_6H_2Me(SH)_3$, prepared by reducing *o*-tolyl-2:4:6-trisulphonyl chloride with tin and hydrochloric acid, forms white needles, m. p. 49—53°, having a characteristic odour. It readily undergoes oxidation, either on exposure to the air or under the action of oxidising agents, with the formation of yellow to yellowish-red products. With lead acetate, it gives a yellow precipitate, which quickly changes to red. In glacial acetic acid solution, it is readily transformed into the original trisulphonyl chloride by the action of chlorine.

The *triacetyl* derivative, $C_6H_2Me(SAc)_3$, forms needles, m. p. 93—95°, and is readily obtained by heating with acetic anhydride and fused sodium acetate. The *trimethyl ether*, $C_{10}H_4S_3$, prepared by the action of diazomethane in ethereal solution, or of methyl iodide in alkaline alcoholic solution, forms slender needles, m. p. 61—63°; it cannot be obtained by the action of hydrogen chloride and methyl alcohol. Trithiomethylphloroglucinol consequently behaves as a non-tautomeric phenol.

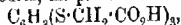
The condensation product with chloroacetic acid,



has m. p. 197—200°; the *ethyl* ester, $C_6H_2Me(S \cdot CH_2 \cdot CO_2Et)_3$, has m. p. 30—35°.

The action of cold concentrated nitric acid (D 1.4) on the trimethyl ether gives rise to the *mononitro*-derivative, $NO_2 \cdot C_6HMe(SMe)_3$, yellow prisms, m. p. 84—87°. With hot concentrated nitric acid or cold fuming nitric acid, a *monosulphoxide* of the above-mentioned nitro-derivative is produced, $NO_2 \cdot C_6HMe \cdot (SMe)_2 \cdot SOMe$, which forms slender, yellow needles, m. p. 178.5—179.5°. The position of the sulphoxide group has not been ascertained. Hot fuming nitric acid also gives rise to a substance, m. p. 235—237°, which requires further investigation.

Trithiophloroglucinol (*Abstr.*, 1909, i, 761) has now been obtained in the form of white needles, m. p. 57—60°. The product,



obtained with chloroacetic acid forms white, silky needles, m. p. 179—180°, from which the *ethyl* ester was obtained as an oil. The trimethyl ether gives the *mononitro*-derivative, $NO_2 \cdot C_6H_2(SMe)_3$, with cold concentrated nitric acid; it forms dark yellow, slender needles, m. p. 148—150°.

T. S. P.

Cholesterol. II. LEO TSCHUGAEFF and W. FOMIN (*Annalen*, 1910, 375, 288—297. Compare this vol., i, 31, 479).—In addition to work already recorded, the paper contains the following results. *Ethyl cholesterylzanthate*, $C_{27}H_{45}O \cdot CS \cdot SEt$, m. p. 141.5°, and the *propyl* ester, m. p. 135°, have almost the same dispersion coefficient as the methyl ester. *Cholesterylzanthamide*, $C_{27}H_{45}O \cdot CS \cdot NH_2$, m. p. 227°, is obtained by digesting the methyl ester with about 10% alcoholic ammonia for many days.

The constitutions of α -cholesterylene, cholesterol, β -cholesterylene,

and cholestane are represented respectively by: $R \begin{smallmatrix} \text{CH} \\ \text{CH}_2 \end{smallmatrix} \text{CH}$,
 $R \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{OH}$, $R \begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix} \text{CH}$, and $R \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH}_2$, where R is
 $(\text{H}_2\text{Pr}^{\beta} \cdot \text{CH}_2)_{17} \text{C}_{17} \text{H}_{35}$

C. S.

Aromatic Fluorine Derivatives and Estimation of Fluorine in the Same. HANS MEYER and ALFRED HUB (*Monatsh.*, 1910, 31, 933—938).—The three fluorobenzoic acids can be prepared readily by the oxidation of the fluorotoluenes with permanganate (compare Hollemann, Abstr., 1905, i, 425). The *o*-acid has m. p. 122°. The corresponding fluorobenzoyl chlorides, $\text{C}_6\text{H}_4\text{F} \cdot \text{COCl}$, can be obtained by the action of thionyl chloride on the acids. They are colourless, strongly refractive liquids with an odour resembling that of benzoyl chloride. The *o*-compound has b. p. 204° and m. p. 4°; the *m*-compound, b. p. 189° and m. p. -30°, and the *p*-compound, b. p. 191—192° and m. p. 9°.

The methyl esters, $\text{C}_6\text{H}_4\text{F} \cdot \text{CO}_2\text{Me}$, have boiling points and melting points as follows: *ortho*, 207°, -20°; *meta*, 194—195°, -10°, and *para*, 197°, 4.5°. Some of these compounds have lower b. p.'s than the unsubstituted derivatives.

o-Fluorobenzamide, $\text{C}_6\text{H}_4\text{F} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from water in colourless needles, m. p. 114°; the *meta*-compound in colourless plates, m. p. 128—129°, and the *para*-compound in colourless needles, m. p. 155°.

In estimating the fluorine in these compounds, the substance is heated with lime in a nickel tube, 40 cm. long and 4—5 mm. diameter, the end of which is closed by means of silver solder. The tube is treated in much the same manner as in the estimation of halogens by the lime method; it is necessary, however, to see that the lime is completely soluble in dilute acetic acid, and a temperature of 1000° must be attained in all parts of the tube. At the end the calcium fluoride is estimated in the usual manner.

J. J. S.

Condensation Products of Anthranilic Acid with Aromatic Aldehydes. HUCC WOLF (*Monatsh.*, 1910, 31, 903—916).—Various aromatic aldehydes have been condensed with anthranilic acid in alcoholic solution in order to determine whether the resulting Schiff's bases exist in stereoisomeric forms (compare Hantzsch and Schwab, Abstr., 1901, i, 378; Anselmino, *ibid.*, 1907, i, 913; Manchot and Furlong, *ibid.*, 1909, i, 805; this vol., i, 33).

Two isomeric forms were observed in the anils obtained by the condensation of the acid with *o*- and *p*-hydroxybenzaldehydes.

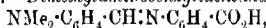
Benzylideneanthranilic acid, $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, crystallises in sulphur-yellow needles, m. p. 128°; *p*-tolylideneanthranilic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, forms lemon-yellow, rectangular plates, m. p. 154°; *o*-nitrobenzylideneanthranilic acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, crystallises in yellow needles, m. p. 172°, and readily turns red on

exposure to the air; the isomeric *para*-compound forms pale yellow plates, m. p. 162°, and the *meta*-derivative, pale yellow needles, m. p. 206°.

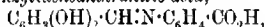
Salicylideneanthranilic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, separates as small, yellow plates, m. p. 193°, when its alcoholic solution is cooled rapidly, otherwise the red modification, which crystallises in stout prisms, m. p. 200°, is obtained. The yellow crystals are transformed into the red when dissolved in amyl alcohol and the solution cooled slowly, or when the solution is cooled quickly and the yellow crystals left in contact with the amyl alcohol mother liquor for several hours. *p*-Hydroxybenzylideneanthranilic acid exists in yellow and red modifications, of which the red is the less stable. The yellow form is more readily soluble in ether than the red, and has m. p. 224°. The isomeric *m*-hydroxy-derivative crystallises in yellow prisms, m. p. 182°.

o-Methoxybenzylideneanthranilic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, forms yellow needles, m. p. 128°; the isomeric *para*-compound crystallises in yellow, rectangular plates, m. p. 142°, which turn red on exposure to the air. *Dimethylaminobenzylideneanthranilic acid*,

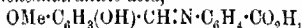


forms brick-red prisms, m. p. 214°.

3:4-Dihydroxybenzylideneanthranilic acid,



crystallises in glistening, red needles, m. p. 226° (decomp.). 4-Hydroxy-3-methoxybenzylideneanthranilic acid,



forms slender, lemon-yellow needles, m. p. 164°. 3:4-Piperonylideneanthranilic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, forms pale yellow, rectangular plates, m. p. 188°. *Cinnamylideneanthranilic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises from toluene or ethyl acetate in yellow prisms, m. p. 156°. When heated at 100°, it begins to turn red, and gives an odour of cinnamaldehyde.

When alcoholic solutions of these anil acids are heated with the equivalent amount of phenylhydrazine for about thirty minutes on the water-bath, the $\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ group is replaced by the



group, and the phenylhydrazones of the aldehydes are obtained.

J. J. S.

Lactonoid Anhydrides of Acylated Amino acids. V. **Lactone of *r*-Benzoylphenylalanine.** ERNST MOHR and Fu. SROSCHER (*J. pr. Chem.*, 1910, [ii], 82, 322—335. Compare this vol., i, 483, 557).—Much of the work has been recorded (Abstr., 1909, i, 581). The ethyl ester, chloride, and anilide of benzoylphenylalanine (Max, Abstr., 1909, i, 926) are conveniently prepared from the lactone; also the anilide, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}\cdot\text{Bz})\cdot\text{CO}\cdot\text{NHPh}$, m. p. 233—234°, from the lactone and aniline in dry ether. *Benzoylphenylalanylglycine*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}\cdot\text{Bz})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 240—242° (decomp., softening at 185°), is obtained from glycine and the lactone of benzoylphenylalanine at 130°, or, better, in aqueous acetone in the presence of sodium hydroxide.

C. S.

o-Aminobenzyl Cyanide [*o*-Aminophenylacetonitrile] and its Conversion into 2-Aminoindole and Indole. ROBERT PSCHORR and GERN. HOPFF (*Ber.*, 1910, 43, 2543—2552).—The conversion of *o*-aminocinnamonnitrile into 2-aminoquinoline by acids or alkalis (P-schorr, *Abstr.*, 1898, i, 491) induced the authors to examine the behaviour of *o*-aminophenylacetonitrile under similar conditions. This substance is conveniently prepared by converting *o*-nitrophenylacetic acid by a suspension of phosphorus pentachloride in ether into the chloride, a solution of which in benzene and ether is converted by ammonia into *o*-nitrophenylacetamide, m. p. 160°; the amide is converted by thionyl chloride into the nitrile, an alcoholic solution of which is reduced by stannous chloride and concentrated hydrochloric acid to *o*-aminophenylacetonitrile, m. p. 72°, which is best isolated by treating an aqueous solution of its stannichloride with 30% sodium hydroxide, whereby the substance separates in almost quantitative yield. The presence of the "activated" methylene group in the ortho-position to the amino group renders derivatives of the substance very liable to intramolecular condensation. Thus a solution of *o*-aminophenylacetonitrile in *N*-hydrochloric acid is converted into *indole-3-carboxylonitrile*, $C_6H_4 \begin{smallmatrix} \text{C(CN)} \\ \text{N} \end{smallmatrix} \text{NH}$, m. p. 140°, whilst a solu-

tion in ether yields by treatment with sodium and amyl formate, *indole-3-carboxylonitrile*, m. p. 178°. This nitrile forms an *acetyl* derivative, m. p. 202°, which is also obtained when *indole-3-alloxime*, m. p. 197—200°, is heated with acetic anhydride.

o-Aminophenylacetonitrile yields a *formyl* derivative,



m. p. 110°, which shows no tendency to intramolecular condensation, and is simultaneously hydrolysed and converted into 2-aminoindole by boiling potassium carbonate; an *acetyl* derivative, m. p. 120°, and a *diacetyl* derivative, m. p. 80°.

By treatment with boiling alcoholic sodium ethoxide in an atmosphere of hydrogen, *o*-aminophenylacetonitrile is converted into 2-aminoindole, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix} \text{C} \cdot NH_2$, which separates from water in

prisms containing H_2O , has a strongly alkaline reaction, is reduced by sodium and alcohol to indole, and forms a *diacetyl* derivative, m. p. 142°, which is converted by aqueous potassium carbonate into 2-*acetyl*-aminoindole, m. p. 167°. When an ethereal solution of 2-aminoindole is treated with ethyl chloroformate, three products are obtained, two of which, m. p. 93° and 160° respectively, are isomeric and contain two carbethoxy-groups, whilst the third has m. p. 145—150° and contains only one carbethoxy-group. The constitution of 2-aminoindole is proved by the fact that Piccini and Salmoni's indole-2-urethane, by treatment with ethyl chloroformate, yields the isomeride, m. p. 93°, containing two carbethoxy-groups, mentioned above. C. S.

Action of Thionyl Chloride on Benzoic Acid. ROBERT STOLLÉ (*Ber.*, 1910, 43, 2471—2473).—By the interaction of thionyl chloride and benzoic acid in carbon tetrachloride solution at the ordinary temperature, α -chlorodiphenylacetic acid is formed. When the con-

stituents are boiled some days in the same solvent, *α-chlorodiphenylacetic anhydride*, $(C_6H_5Cl-CO)_2O$, is formed, m. p. 129°. This compound also arises when *α-chlorodiphenylacetic acid* is warmed with thionyl chloride. With aniline in ethereal solution, *α-anilindiphenylacetic acid*, m. p. 168°, and *α-anilindiphenylacetic anhydride*, crystallising in minute needles, m. p. 181°, and insoluble in sodium hydroxide, are formed.

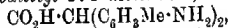
A by-product of the action of thionyl chloride on benzoic acid crystallises in compact crystals insoluble in sodium carbonate, m. p. 119°. This is possibly *tetraphenyldiglycolyl chloride*, $C_{28}H_{20}O_2Cl_2$; it forms an anilide, m. p. 134°.

On shaking chlorodiphenylacetic anhydride in ether with sodium carbonate, an amorphous compound, probably benzoic anhydride, m. p. about 90°, is obtained. When heated with yellow mercuric oxide, chlorodiphenylacetic anhydride yields benzilide, m. p. 194°, which probably has the constitution of tetraphenyldiglycolic anhydride.

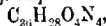
E. F. A.

Action of Dichloroacetic Acid on Aniline and its Homologues. III. GUSTAV HELLER with SALO ASCHKENASI (*Annalen*, 1910, 375, 261—288. Compare Abstr., 1908, i, 216).—The paper contains a repetition of some of the earlier work in order to controvert Ostromisslensky's views of the course of the reaction between dichloroacetic acid and aniline or its homologues (Abstr., 1908, i, 82, 888, 889).

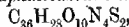
The reaction between dichloroacetic acid and *p*-anisidine furnishes the only case in which the initial product of the reaction has been isolated; *di-p-anisidinoacetic acid*, $CO_2H \cdot CH(NH \cdot C_6H_4 \cdot OMe)_2$, m. p. 201—202°, forms a *hydrochloride*, $C_{16}H_{18}O_2N_2 \cdot HCl$, m. p. about 215°, cannot be diazotised or benzoylated, and does not form a nitrosoamine. The product of the reaction between dichloroacetic acid and *o*-toluidine is not *o*-methylaminophenyl-*o*-toluidinoacetic acid (Ostromisslensky, *loc. cit.*), but 2:2'-*diaminoditolyl-4:4'-acetic acid*,



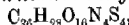
since it requires 2 mols. of sodium nitrite for diazotisation, and the diazotised product yields *bis-β-naphtholazodi-o-tolylacetic acid*,



m. p. 195°, *bis-6-sulpho-β-naphtholazodi-o-tolylacetic acid*,

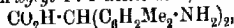


and *bis-3:6-disulpho-β-naphtholazodi-o-tolylacetic acid*,



with *β*-naphthol, *β*-naphthol-6-sulphonic acid, and *β*-naphthol-3:6-disulphonic acid respectively. 2:2'-Diaminoditolyl-4:4'-acetic acid yields only a *monobenzoyl* derivative, m. p. 242—243°, by the Schotten-Baumann method; when benzoylated in the presence of sodium hydrogen carbonate, it yields a mixture of the preceding compound and an anhydro-derivative, $C_{23}H_{20}O_2N_2$, thereof.

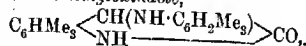
2:2'-*Diamino-di-m-xylyl-4:4'-acetic acid*,



m. p. 241°, obtained from aqueous potassium dichloroacetate, sodium acetate, and *m*-2-xylydine on the water-bath, or from an acetic acid solution of the base and glyoxylic acid at the ordinary temperature,

forms a *dibenzoyl* derivative, $C_{22}H_{20}O_4N_2$, m. p. 272° (decomp.), with benzoyl chloride in aqueous potassium hydroxide, an *anhydrobenzoyl* derivative, $C_{25}H_{24}O_2N_2$, unchanged at 300° , with benzoyl chloride in cold pyridine, and combines, after being diazotised, with β -naphthol-6-sulphonic acid in sodium carbonate solution to form a normal *bisazo*-compound, $C_{28}H_{28}O_{10}N_4S_2$, the combination in a solution of an alkali hydroxide yielding a black substance.

The usual reaction between dichloroacetic acid and ψ -cumidine yields 3- ψ -cumidino-4:5:7-trimethyloxindole,



decomp. 205° ; this is oxidised by iodine in glacial acetic acid to 4:5:7-trimethylisatin, $C_6HMe_3 \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \text{CO}$, m. p. 276° , which forms red needles, yields a *phenylhydrazone*, m. p. 248° , and is so stable to alkalis that the pyrrole nucleus is only ruptured at 50° .

The product of the direct action of dichloroacetic acid on aniline is not 4:4'-diaminodiphenylacetic acid (Ostrowskislensky, *loc. cit.*), but its hydrochloride (Heller, Abstr., 1909, i, 20); the free acid has m. p. 195° , forms a *diacetyl* compound, m. p. 231° , and yields a *dibenzoyl* derivative, decomp. 256° , with benzoyl chloride and sodium hydroxide, and an *anhydrobenzoyl* derivative, $C_{21}H_{16}O_2N_2$, softening at 225° , with benzoyl chloride in cold pyridine. The product obtained by the addition of a dilute acetic acid solution of aniline to aqueous glyoxylic acid is aniline anilglyoxylate, not dianilinoacetic acid (Ostrowskislensky, Abstr., 1908, i, 889), because only 1 mol. of aniline is eliminated by cold sodium carbonate.

C. S.

Preparation of Oxyaryluurethane Carbamido- and Thio-carbamido-cinnamic Acid Esters. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 224107).—Cinnamic acid esters of the

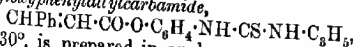
general formula $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot R \cdot NH \cdot C \begin{array}{c} X \\ \ll Y \end{array}$ (where R is an aromatic radicle, X oxygen or sulphur, Y an alkyloxy, amino, or alkyl-amino-group) are readily prepared when cinnamoyl chloride is heated with *p*-hydroxyphenyl-carbamide or urethanes; they are of great value in the treatment of tubercular complaints, and in surgery.

p-Cinnamoyloxyphenylcarbamide, colourless needles, m. p. 203° , is prepared by heating (or allowing to remain at the ordinary temperature) cinnamoyl chloride with *p*-hydroxyphenylcarbamide in aqueous alkaline solution.

m-Cinnamoyloxyphenylcarbamide has m. p. $204-205^\circ$.

p-Cinnamoyloxyphenylurethane, colourless needles, m. p. $150-151^\circ$, is prepared from the foregoing acid chloride and *p*-hydroxyphenylurethane, $OH \cdot C_6H_4 \cdot NH \cdot CO_2Et$. *o*-Cinnamoyloxyphenylurethane has m. p. $101-102^\circ$.

p-Cinnamoyloxyphenylallylcarbamide,



m. p. $129-130^\circ$, is prepared in analogous manner from *p*-hydroxyphenylallylthiocarbamide in acetone solution.

Cinnamic anhydride, or the acid in the presence of phosphoryl

chloride, can also be employed for this condensation, likewise other hydroxyphenylcarbamido-derivatives. F. M. G. M.

Melting Point of Granules of Salol. P. N. PAWLOFF (*Zeitsch. physikal. Chem.*, 1910, 74, 562—566. Compare Abstr., 1908, ii, 927).—The relationship between the melting point of salol particles and their magnitude has been further investigated by heating commercial salol for long periods at constant temperatures, and determining by microscopic observation the surface area of the largest crystals which formed as a result of fusion and subsequent crystallisation. It was found necessary to heat for about two and a-half hours in order to obtain the maximum size of crystals.

The more fusible portion was investigated between 34·8° and 37·8° by the method described. The maximum crystal at 37·8° had a surface of 1296 sq. μ ; the maximum formed at 34·8° a surface of 228 sq. μ . The less fusible portion was investigated between 39° and 41°. At the former temperature, particles of surface 200 sq. μ , at the latter temperature, particles of surface 1328 sq. μ , remain unaltered. The relative size of the crystals cannot readily be determined, but from the data obtained for the less fusible portion it is estimated that when the specific surface is increased one hundred times by dividing up the particles, the melting point is lowered by 2·8°. G. S.

Preparation of Monoiodosalicylic Acids or its Nuclear Homologues. MAX HAASE (D.R.-P. 224536. Compare Lassar-Cohn and Fritz Schultze, Abstr., 1905, i, 893).—The methods that have previously been employed for the preparation of monoiodosalicylic acids have given poor yields and impure products; the one now described is that whereby an alkaline solution of sodium salicylate is slowly treated with a very slight excess of iodine dissolved in potassium iodide at the ordinary temperature and with continual stirring; colourless needles, m. p. 197°, were obtained. Three iodosalicylic acids with m. p.'s 198°, 196°, and 199·5° have previously been described in the literature. F. M. G. M.

Preparation of Amides of Monoiodosalicylic Acid and its Homologues. MAX HAASE (D.R.-P. 224346).—The amides of iodosalicylic acid (or other hydroxycarboxylic acids) can be readily prepared by treating the respective acid amide with potassium iodide and iodine in alkaline solution and allowing the mixture to remain at the ordinary temperature.

Iodosalicylamide, colourless leaflets, m. p. 230—231°, is sparingly soluble in hot water, and of therapeutic value. F. M. G. M.

Preparation of 5-Iodo-2-acetoxybenzoic Acid. MAX HAASE (D.R.-P. 224537).—The attempted preparation of iodoacetoxybenzoic acid from acetoxybenzoic acid results in the elimination of the acetyl group; it is now found that acetylation of iodosalicylic acid yields the required product.

5-Iodo-2-acetoxybenzoic acid, colourless needles, m. p. 175°, is prepared by boiling iodosalicylic acid with acetic anhydride in the presence

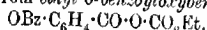
of anhydrous sodium acetate during three hours; it is a very important therapeutic agent, comparing favourably with *o*-acetoxybenzoic acid (aspirin) in being tasteless and less readily hydrolysed.

F. M. G. M.

Preparation of Acylsalicylic [*o*-Acyloxybenzoic] Anhydrides. ALFRED EINHORN (D.R.-P. 224844).—When the carbonyl esters of acylsalicylic acids (usually oils) having the general formula $OX \cdot C_6H_4 \cdot CO \cdot O \cdot CO_2R$ ($R = \text{alkyl}$; $X = \text{acyl}$) are heated, they yield the corresponding crystalline acyl salicylic anhydride.

o-Acetoxybenzoic anhydride, glistening needles, *m. p.* 85°, is prepared by heating *o*-acetoxybenzoic acid with ethyl chlorocarbonate in benzene or ethereal solution in the presence of a tertiary base, such as pyridine; the ethyl *o*-acetoxybenzoylcarbonate, $OAc \cdot C_6H_4 \cdot CO \cdot O \cdot CO \cdot OEt$, is isolated in the form of a viscid oil, which, when heated during ten to twenty-four hours on the water-bath, is transformed into the foregoing anhydride.

Benzoxyloxybenzoic anhydride, prismatic needles, *m. p.* 109—111°, is similarly obtained from ethyl *o*-benzoxyloxybenzoylcarbonate,

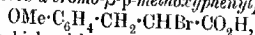


o-Cinnamoyloxybenzoic acid anhydride, slender needles, *m. p.* 110—112°, from ethyl *o*-cinnamoyloxybenzoylcarbonate, *m. p.* 53—55°. These compounds are of therapeutic value.

F. M. G. M.

The *N*-Methyl Derivatives of Phenylalanine and Tyrosine. ERNST FRIEDMANN and S. GUTMANN (*Biochem. Zeitsch.*, 1910, 27, 491—497).—In connexion with earlier experiments on the behaviour of methylated amino-acids in the animal body (Friedheim, *Abstr.*, 1908, i, 205), the authors have prepared the methyl derivatives of the aromatic amino-acids occurring in proteins. *α*-Methylamino-*β*-phenylpropionic acid (phenyl-*N*-methylalanine), $CH_3Ph \cdot CH(NHMe) \cdot CO_2H$, prepared from aqueous methylamine and *α*-bromo-*β*-phenylpropionic acid, crystallises in three-sided plates subliming at 252—254° (decomp.).

p-Methoxybenzylmalonic acid, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H)_2$, prepared by reducing anisylidenemalonic acid with sodium amalgam by Knoevenagel's condensation, crystallises in large, irregular plates, *m. p.* 118.5° (decomp.). On treatment with bromine, it yields the *α*-bromo-derivative, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CBr(CO_2H)_2$, which crystallises in four-sided leaflets decomposing at 153°. On heating at 120—130° with a little water, this gives *α*-bromo-*β*-*p*-methoxyphenylpropionic acid,



a brown, viscid oil, which with methylamine furnishes *α*-methylamino-*β*-*p*-methoxyphenylpropionic acid, crystallising in colourless scales, *m. p.* 254—257° (decomp.). This, on hydrolysis with hydrobromic acid, gives *α*-methylamino-*β*-*p*-hydroxyphenylpropionic acid (*N*-methyltyrosine), $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NHMe) \cdot CO_2H$, which crystallises in bunches of blunt needles, *m. p.* 315°.

G. S. W.

2-Naphthol-3-carboxylic Acid and its Condensation with Benzaldehyde. FRANZ FRIEDL (*Monatsh.*, 1910, 31, 917—932. Compare J. Schmid, *Abstr.*, 1893, i, 475; Möhlau, *ibid.*, 1896, i, 43).—The ketonic formula for 2-naphthol-3-carboxylic acid is some-

what analogous to that of benzyl methyl ketone; the condensation of benzaldehyde with methyl 2-naphthol-3-carboxylate in the presence of hydrogen chloride has been studied, and has been found to be of the same type as the condensation of benzyl methyl ketone and benzaldehyde in the presence of hydrogen chloride (Goldschmiedt and Krczmar, Abstr., 1901, i, 40), the resulting compound being methyl α -chloro-

1-benzyl-2-naphthol-3-carboxylate, $C_6H_5 \begin{smallmatrix} C(CHPhCl):C:OH \\ CH= \\ C:CO_2Me \end{smallmatrix}$ or the

tautomeric ketone. The halogen atom in this compound is extremely reactive, and can be replaced readily by hydroxyl, methoxy-, phenoxy-, amino-, and anilino-groups (compare Braun, this vol., i, 479).

Methyl 2-naphthol-3-carboxylate has m. p. 73°.

Methyl α -chloro-1-benzyl-2-naphthol-3-carboxylate, $C_{19}H_{15}O_3Cl$, formed when dry hydrogen chloride is passed into a solution of methyl 2-naphthol-3-carboxylate in benzaldehyde at 0°, and the saturated solution kept for twenty-four hours, crystallises from perfectly dry benzene in microscopic prisms, m. p. 160–161°. At higher temperatures it loses hydrogen chloride, and at 220–225° is completely decomposed.

The corresponding *bromo-derivative*, $C_{19}H_{15}O_3Br$, has m. p. 183°; the *hydroxy-derivative*, *methyl 1- α -hydroxybenzyl-2-naphthol-3-carboxylate*, $C_{19}H_{16}O_4$, crystallises from benzene in pale yellow, glistening prisms, m. p. 173–174°. *Methyl 1- α -acetoxybenzyl-2-naphthol-3-carboxylate*, obtained by the action of acetic anhydride on the hydroxy-compound, forms pale yellow prisms, m. p. 136–137°. *Methyl α :2-diacetoxy-1-benzyl-3-naphthoate* has m. p. 70–73°, and decomposes at 85°. *Methyl 1- α -methoxybenzyl-2-naphthol-3-carboxylate*, $C_{20}H_{18}O_4$, prepared by the action of methyl alcohol on the chloro-derivative, crystallises from a mixture of benzene and alcohol in yellow, flat prisms, m. p. 177°. The corresponding *ethoxybenzyl derivative*, $C_{21}H_{20}O_6$, has m. p. 116–117°, and the *phenoxybenzyl compound*, $C_{23}H_{20}O_6$, m. p. 188°.

Methyl 1- α -aminobenzyl-2-naphthol-3-carboxylate, $C_{19}H_{17}O_3N$, crystallises from a mixture of chloroform and alcohol in yellow, microscopic prisms, m. p. 220°; the corresponding *anilinobenzyl derivative*,

$C_{25}H_{21}O_3N$,
crystallises in small prisms, m. p. 214°, and yields a *hydrochloride*,

$C_{25}H_{21}O_3N \cdot HCl$,
in the form of colourless crystals, m. p. 175° (decomp.).

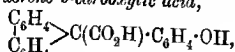
1-Benzyl 2-naphthol-3-carboxylic acid, $C_{18}H_{14}O_3$, obtained by heating the methyl ester of the chloro-acid with hydriodic acid, crystallises in lemon-yellow needles, m. p. 224°, and gives a blue coloration with ferric chloride; the *acetyl derivative*, $C_{20}H_{16}O_4$, forms colourless, glistening needles, m. p. 166°, and the *methyl ester*, $C_{19}H_{16}O_3$, microscopic, yellow needles, m. p. 107°.

Most of the compounds are probably equilibrium mixtures of the ketonic and enolic forms. J. J. S.

Condensation of Diphenyleneglycollic Acid with Phenols and Phenol Ethers. AUGUSTIN BISTRZYCKI and FRANZ VON WERRA (*Ber.*, 1910, 43, 2496–2505).—It was shown previously (Bistrzycki,

Abstr., 1901, i, 716) that benzilic acid condenses with phenols, and that the tertiary acids, formed readily on solution in concentrated sulphuric acid, lose carbon monoxide, forming carbinols. Diphenyleneglycollic acid likewise condenses with phenols, but the acids formed are only decomposed at high temperatures by concentrated sulphuric acid, and sulphonic acids of the expected carbinols are obtained.

9-*p*-Hydroxyphenylfluorene-9-carboxylic acid,



prepared by condensation of diphenyleneglycollic acid with phenol, is obtained in microscopic, colourless, obliquely-cut plates from benzene containing a molecule of the solvent; it sinters and loses this at 98°, the residue becoming solid and getting red, m. p. 177° (decomp.). The benzene is difficult to remove; a preparation from alcohol had m. p. 178° (decomp.).

A by-product of the condensation is the lactone of 9-*o*-hydroxyphenylfluorene-9-carboxylic acid, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{O} < \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} > \text{O}$, which crystallises in microscopic, doubly refractive pyramids, m. p. 213°. On heating *p*-hydroxyphenylfluorene-9-carboxylic acid in a stream of air at 200°, carbon dioxide is eliminated, and 9-*p*-hydroxyphenylfluorene is formed, crystallising in colourless needles, m. p. 178—179° (decomp.), identical with the product obtained by Bistrzycki and Vlekke (*Diss.*, 1905) from phenol and fluorenyl alcohol.

9-*p*-Acetoxyphenylfluorene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$, obtained on boiling *p*-hydroxyphenylfluorene-9-carboxylic acid with acetic anhydride, crystallises in slender needles, m. p. 139—140°.

9-*p*-Hydroxy-*m*-tolylfluorene-9-carboxylic acid, from diphenyleneglycollic acid and *o*-cresol, crystallises in matted prisms, m. p. 183—184° (decomp.). The corresponding lactone of 9-*o*-hydroxy-*m*-tolylfluorene-9-carboxylic acid separates in colourless plates, m. p. 147.5—149°.

9-*p*-Hydroxy-*m*-tolylfluorene, obtained by heating the above carboxylic acid at 220°, crystallises in colourless, six-sided prisms, m. p. 165—166° (decomp.). The acetate crystallises in rosettes of colourless prisms, m. p. 95—97°.

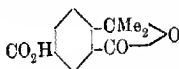
Diphenyleneglycollic acid condenses with *m*-cresol, forming a *p*-hydroxy-acid, which crystallises with difficulty. At the same time, 9-*o*-hydroxy-*p*(1)-tolylfluorene-9-carboxylic acid lactone is obtained; it separates in aggregates of obliquely-cut prisms, m. p. 192°. The lactone of 9-(2'-hydroxy-5'-tolyl)fluorene-9-carboxylic acid is the only product of the condensation with *p*-cresol. It is at first obtained as a red oil, and crystallises in transparent plates with many faces, m. p. 138°.

9-*p*-Methoxyphenylfluorene-9-carboxylic acid, prepared by condensation with anisole, forms a crust of colourless, microscopic plates, m. p. 144—145° (decomp.). 9-*p*-Methoxyphenylfluorene, obtained on heating the foregoing compound at 160°, forms colourless prisms, m. p. 21—22°.

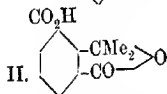
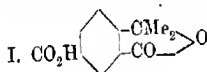
E. F. A.

Synthesis of *iso*Propylisophthalic Acid and Dimethylphthalidecarboxylic Acid. GUIDO BARGELLINI (*Gazzetta*, 1910, 40, ii, 27—36).—The position assigned to the side-chain in santonin with respect to the ketonic group depends on the constitution of the dimethylphthalidecarboxylic acid obtained from it by Cannizzaro and Gucci (Abstr., 1893, i, 665). The acid has therefore been synthesised.

By nitrating cuminic acid with fuming nitric acid, 3-nitrocuminic acid (3-nitro-4-propylbenzoic acid) is obtained in prisms, m. p. 156—157°. Reduction with ammonium sulphide yields 3-aminocuminic acid, which crystallises in a labile modification, m. p. 104°, and a stable modification, m. p. 129°. Diazotisation, followed by heating with a solution of potassium copper cyanide, yields an uncrystallisable 3-cyanocuminic acid. This acid is very difficult to saponify, and it is necessary to convert it into the *amide*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{Pr}^2\cdot\text{CO}\cdot\text{NH}_2$, by boiling with sodium hydroxide. The product has m. p. 265°, and is converted into *iso*propylisophthalic acid by dissolving in concentrated sulphuric acid and adding sodium nitrite. The product crystallises from boiling water, and has m. p. 236°. Oxidation with potassium permanganate in alkaline solution converts it into dimethylphthalidecarboxylic acid (annexed formula), which is identical with that prepared from santonin. C. H. D.



A New Synthesis of Dimethylphthalidecarboxylic Acid. GUIDO BARGELLINI and G. FORL-FORTI (*Gazzetta*, 1910, 40, ii, 74—89. Compare preceding abstract).—An attempt has been made to prepare the acid (II) for comparison with the acid obtained from santonin, which is assumed to have the constitution (I). The method



selected was that of converting 3-nitrophthalic anhydride into the dimethylphthalide, and then of replacing the nitro-group by carboxyl. It is found, however, that the neighbourhood of the nitro-group prevents the anhydride from reacting with Grignard's reagent.

When dimethylphthalide is nitrated the nitro-group replaced by carboxyl, an acid is obtained which is identical with that from santonin. The nitro-group is shown to occupy the para-position to the phthalide group, as it yields a nitrile which is readily saponified, whilst an *o*-nitrile would be difficult to saponify, as in the case of cyanocuminic acid. The nitration of methylphthalide (Giebe, Abstr., 1897, i, 63) and of diethylphthalide (Bauer, Abstr., 1904, i, 417; 1908, i, 274) is also known to yield para-derivatives. An attempt to prove the constitution directly by conversion into the hydroxy-compound, reduction, and distillation with lime, in order to examine the *isopropylphenol* produced, failed owing to the smallness of the yield obtained on reducing the hydroxyl compound with phosphorus and hydriodic acid.

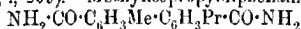
The reduction of nitrodimethylphthalide with aluminium amalgam yields, instead of the amino-compound, an orange-yellow, crystalline

substance, m. p. 225—230°, devoid of basic properties. 5-Aminodimethylphthalide, $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CMe}_2\\\text{CO}\end{smallmatrix}\rangle\text{O}$, obtained by reduction with stannous chloride, forms white leaflets, m. p. 117°. The *picrate* has m. p. 198—200°, softening at 192°. The *acetyl* derivative has m. p. 172—175°.

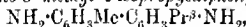
5-Hydroxydimethylphthalide, obtained by the diazo-reaction, forms white needles, m. p. 151—153°; its *acetyl* derivative has m. p. 76—78°; the *methyl ether* softens at 92—93° and melts at 98—99°.

In the attempt to prepare cyanodimethylphthalide by the diazo-reaction, an additive compound, m. p. 211—212°, is obtained, from which the compound may be isolated by heating in carbon dioxide, when cuminaldehyde volatilises, and a residue of 5-cyanodimethylphthalide, softening at 154° and melting at 159—160°, is obtained. Hydrolysis converts it into dimethylphthalidecarboxylic acid, identical with that obtained by other methods. C. H. D.

Retene. PAUL LUX (*Monatsh.*, 1910, 31, 939—949. Compare Bucher, this vol., i, 239).—Methylisopropylidiphenamide,

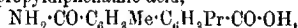


(this vol., i, 239), crystallises from benzene, and has m. p. 204—206° (corr.). When treated with bromine and potassium hydroxide solution, it yields 2:2'-diamino-3'-methyl-4-isopropylidiphenyl,



which forms colourless crystals, m. p. 89—90° (corr.). The *hydrochloride*, $\text{C}_{16}\text{H}_{20}\text{N}_2\cdot 2\text{HCl}$, melts above 240°. A better yield of the diamine can be obtained by using Jeffrey's method (*Abstr.*, 1897, i, 315). The *urethane*, $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, forms colourless crystals, m. p. 239—241° (decomp.), and when heated with slaked lime yields the diamine. It has not been found possible to diazotise the diamine and obtain the corresponding hydrocarbon; the product formed appears to be *methyl isopropylcarbazole*, $\text{C}_{16}\text{H}_{17}\text{N}$. It crystallises in glistening prisms, m. p. 124° (corr.), and yields a *picrate*, m. p. 166—167° (corr.).

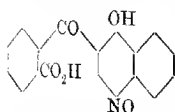
3'-Methyl-4-isopropylidiphenamic acid,



has m. p. 198—199°.

J. J. S.

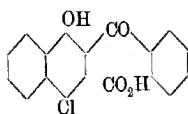
Preparation of *o*-4-Nitroso-1-hydroxynaphthoylbenzoic Acid. ANILFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 223306).—*o*-4-Nitroso-1-hydroxy- β -naphthoylbenzoic acid (annexed formula) is prepared by treating finely-



powdered *o*-1-hydroxy- β -naphthoylbenzoic acid with a concentrated solution of sodium nitrite, and keeping the paste well stirred at a temperature of 45° during six or eight hours, with further additions of water as necessary to keep it at a workable consistency. It forms sulphur-yellow crystals, m. p. 195° (the *sodium salt* is sparingly soluble), and on reduction yields *o*-4-amino-1-hydroxy- β -naphthoylbenzoic acid.

F. M. G. M.

Preparation of *o*-4-Chloro-1-hydroxy- β -naphthoylbenzoic Acid. ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 224538).—The action of ordinary



chlorinating agents on *o*-1-hydroxy- β -naphthoylbenzoic acid is violent and leads to the formation of mixed products; it is now found that sulphuryl chloride in ethereal solution and at a low temperature gives a good yield of 4'-chloro-1'-hydroxy- β -naphthoyl-*o*-benzoic acid.

bright yellow prisms, m. p. 211°.

F. M. G. M.

Action of Light on Benzaldehyde in the Presence of Iodine. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 300—302. Compare this vol., i, 389, 561).—Among the products of this reaction, isobenzil, $\text{COPh}\cdot\text{O}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{COPh}$, has now been identified.

R. V. S.

Action of Light on *p*-Tolualdehyde in the Presence of Iodine. LUIGI MASCARELLI and G. RUSSI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 239—242. Compare this vol., i, 389, 561).—The results obtained were similar to those already recorded in the case of benzaldehyde. The aldehyde when exposed to light in the presence of iodine for three years yielded (1) *p*-toluic acid; (2) a trimeric *tolualdehyde*, forming thin, colourless, prismatic crystals, m. p. 215°; (3) *p*-tolyl *p*-toluate, a pale yellow oil, b. p. 213—217°/15 mm., identical with that prepared by the Schotten-Baumann reaction (b. p. 224—228°/20—21 mm.).

R. V. S.

Nature of the Catalytic Action of Zinc Chloride by the Condensation of Aromatic Ketones with Amines. G. REDDELIEN (*Ber.*, 1910, 43, 2476—2480. Compare this vol., i, 118).—Benzophenone condenses readily with aniline and its derivatives in presence of anhydrous zinc chloride, or of the corresponding zinc chloride amine salt, for example, aniline zinc chloride, $\text{ZnCl}_2(\text{NH}_2\text{Ph})_2$. When the amine forms no additive compound with zinc chloride (for example, *m*-nitroaniline, *m*-aminophenol), no condensation takes place. The zinc chloride amine compounds are not hygroscopic, and they act only as amine carriers, whereas the elimination of water from compounds, $\text{OH}\cdot\text{CR}_2\cdot\text{NHR}$, is brought about by the high temperature of the reaction. There is no interaction when benzophenone and aniline zinc chloride alone are heated at 160°, reaction immediately beginning when aniline is introduced. Benzophenoneanil is partly decomposed by zinc chloride at 160° with the formation of the compound $\text{ZnCl}_2(\text{NH}_2\text{Ph})_2$.

The additive compounds of zinc chloride with the toluidines, xylydine, and phenylenediamine also act as catalysts. Anhydrous zinc chloride also acts as a condensing agent when more is used at a higher temperature, and the reaction is continued for a longer period. It acts not as a catalyst, but in withdrawing water.

On heating acetophenone with aniline in presence of zinc chloride, the chief product is triphenylbenzene, m. p. 170°. When zinc chloride

aniline is used, acetophenoneanil is obtained as a pale yellow oil, b. p. $198-200^{\circ}/37$ mm., solidifying to colourless crystals, m. p. 41° . It dissolves in concentrated sulphuric acid with an intense yellow coloration.

The following keto-imines have been condensed by means of zinc chloride amine or zinc chloride:

Bis-diphenylmethylene-p-phenylenediamine, $\text{CPh}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CPh}_2$, crystallises in golden-yellow, jagged plates, m. p. 180° . *p-Phenylenediamine zinc chloride*, $\text{ZnCl}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, forms bunches of colourless, microscopic needles.

Fluorenoneanil, $\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{NPh}$, separates in golden-yellow needles grouped in rosettes, m. p. 89° . *Fluorenone-p-toluidine* forms lustrous, golden-yellow needles, m. p. 124° .

Diphenylenemethylene-p-aminophenol forms large, lustrous, dark brown plates, which become yellow on heating, m. p. $218-219^{\circ}$.

Bis-diphenylenemethylene-p-phenylenediamine crystallises in lustrous, red needles, m. p. 278° .
E. F. A.

Keto-anils. MAX BUSCH and FERD. FALCO (*Ber.*, 1910, 43, 2557-2564).—The easy production of keto-anils, $\text{NR}\cdot\text{CR}'\text{R}''$, by the interaction of benzanilideimino-chloride and magnesium alkyl halogenides in ether (this vol., i, 729) led the authors to hope they had discovered a satisfactory method of testing the Hantzsch-Werner hypothesis of the stereoisomerism of trivalent nitrogen compounds (compare Straus and Ackermann, this vol., i, 241). *Deoxybenzoinanil*, $\text{NPh}\cdot\text{CPh}\cdot\text{CH}_2\text{Ph}$, m. p. 89° , is ultimately obtained by the interaction of benzanilideimino-chloride and an excess of magnesium benzyl chloride; it forms slender needles and decomposes easily in alcoholic solution, especially by treatment with dilute sulphuric acid, into deoxybenzoin and aniline. When heated above 100° for two to three hours it is oxidised to a great extent to benzanil; by exposing its solution in petroleum to sunlight for five to six hours, benzanilide and benzanil are formed. (Equal molecular quantities of benzanilideimino-chloride and magnesium benzyl chloride react in ether ultimately to form chiefly diphenylbenzenylamidine.)

Phenyl α -naphthyl ketoneanil, $\text{NPh}\cdot\text{CPh}\cdot\text{C}_{10}\text{H}_7$, obtained from the product of the reaction between magnesium α -naphthyl bromide and benzanilideimino-chloride in ether, exists in two forms: long, monoclinic leaflets, m. p. 101° , and triclinic prisms, m. p. 95° . The former are obtained from concentrated, the latter from dilute, solutions, and either can be obtained from a solution of the other by inoculation. Despite the difference of m. p. and of crystalline form, the two substances are regarded as dimorphous forms of an individual substance and not as stereoisomerides, because they are identical as regards colour, solubility, and chemical behaviour (*hydrochloride*, m. p. $187-188^{\circ}$; *picrate*, m. p. 165°).
C. S.

m-p-Ditolyl Ketone. JAMES LAVAUX and MAURICE LOMBARD (*Bull. Soc. chim.*, 1910, [iv], 7, 913-915).—The action of methylene chloride on toluene in presence of aluminium chloride leads to the production of a mixture of hydrocarbons, which on oxidation furnishes

m-p-ditolyl ketone as one product. The ketone and some of its derivatives are described.

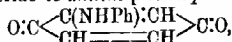
The yield of hydrocarbons in the condensation is about 60% of the theoretical, and the product consists of ditolylmethane and dimethylanthracene in the proportion 20:1. The ditolylmethane boils at 288–290°, and on oxidation with chromic acid in acetic acid furnishes *benzophenone-3:4'-dicarboxylic acid*, m. p. 337° (corr.), which crystallises from alcohol in small needles, and *m-p*-ditolyl ketone, m. p. 70.5°, which forms acicular crystals from boiling alcohol, and is readily soluble in organic solvents, particularly in chloroform; the *oxime*, m. p. 128–129°, forms needles, and the *semicarbazone*, m. p. 183° (approx.), crystallises from alcohol.

The constitution of the ketone is established by the fact that it yields on fusion with potassium hydroxide, *m*- and *p*-toluic acids, and the amides of these two acids on treatment with sodamide. T. A. H.

Reaction between *p*-Benzoquinone and Hydrogen Chloride. ARTHUR MICHAEL and PHILIP H. CORR (*J. pr. Chem.*, 1910, [ii], 82, 297–306).—The author takes exception to Thiele's and to Posner's explanation of the action of hydrogen chloride or bromide on *p*-benzoquinone by the theory of partial valency; this theory requires that halogenated quinols should be the first products of the reaction, whereas the author shows that in chloroform or carbon tetrachloride the initial product is quinhydrone or a mixture of quinhydrone and chloroquinone. C. S.

Mechanism of Quinone Reactions. Reply to Posner. ARTHUR MICHAEL (*J. pr. Chem.*, 1910, [ii], 82, 306–321).—The author gives a further reply to Posner's criticisms (Abstr., 1904, i, 1029; 1909, i, 809) of his explanations of the reactions between *p*-benzoquinone and hydrogen chloride, aniline, and thiophenol (Abstr., 1904, ii, 164; 1909, i, 494). C. S.

Quinonoid Compounds. XXIII. Oxidation of Aniline. RICHARD WILLSTÄTTER and RIKŌ MAJIMA (*Ber.*, 1910, 43, 2588–2593).—A new example of ortho-condensation during the oxidation of aniline is furnished by the use of ferric chloride. A solution of aniline in 6% sulphuric acid is treated at 30° with a concentrated solution of ferric chloride (equiv. to 2½O), whereby a mixture of aniline-black and dianilinobenzoquinone is produced, from which the latter may be isolated by sublimation in a vacuum, by extraction with boiling chloroform, or by extraction with nitrobenzene and sublimation at 15 mm. in carbon dioxide of the brown, crystalline product obtained from the cold solution. By reduction with tin and warm hydrochloric acid, dianilinobenzoquinone is converted into anilinoquinol, a solution of which in *N*-hydrochloric acid is oxidised by careful treatment with *N*/10-ferric chloride to *anilino-p-benzoquinone*,



m. p. 117–118°. This substance, which is much more intensely coloured than more complex anilinobenzoquinones, forms glistening,

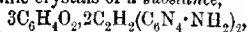
bronze plates, which are brownish-yellow by transmitted light, gives intensely red solutions, is stable to sulphurous acid, and is reduced by zinc and acetic acid to dihydroxydiphenylamine.

An aqueous 2% solution of aniline is oxidised by Caro's method with saturated potassium persulphate in the presence of calcium carbonate; the red, crystalline product, m. p. 252°, which is regarded as *dianilino-*

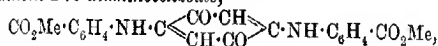
p-benzoquinonimine, $\text{NH} \cdot \text{C} \begin{array}{c} \text{C}(\text{NHPh}) \cdot \text{CH} \\ \text{CH} \cdot \text{C}(\text{NHPh}) \end{array} \text{C} \cdot \text{O}$, yields dianilino-benzoquinoneanil with aniline and acetic acid, is very stable to lead dioxide and sulphuric acid, and dissolves in concentrated sulphuric acid with a brownish-violet colour, which turns violet by the addition of alcohol and warming.

C. S.

Action of *p*-Benzoquinone on Diamines and Esters of Amino-acids. WILHELM SIEGMUND (*J. pr. Chem.*, 1910, [ii], 82, 409—414. Compare Schlenk, *Abstr.*, 1909, i, 807; Fischer and Schrader, this vol., i, 270).—By cooling a hot solution of *p*-benzoquinone (2 mols.) and diaminodiphenylmethane (1 mol.) in a little benzene, glistening, black, rhombic plates of a substance, $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, m. p. 72—73°, are obtained, which gives a violet coloration with concentrated sulphuric acid. In a similar way, *p*-benzoquinone and diaminostilbene yield brownish-black, metallic crystals of a substance,



m. p. 130°, which gives a yellow coloration with sulphuric acid. A benzene solution of *p*-benzoquinone and methyl *p*-aminobenzoate in the proportion 3 : 2 yields, after the addition of petroleum, dark red leaflets of the substance, $\text{C}_6\text{H}_4\text{O}_2 \cdot 2\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, m. p. 83°, which by prolonged boiling with *p*-benzoquinone in alcohol is converted into methyl *p*-benzoquinone-2 : 5-diaminobenzoate,

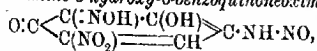


which crystallises in brown needles, and decomposes when heated.

C. S.

Stable Primary Nitrosoamine. GUSTAV HELLER and APOSTOLOS SOURLIS (*Ber.*, 1910, 43, 2581—2588).—4 : 6-Dinitroresorcinol (which forms a *diacetate*, m. p. 139°, and a *dibenzoate*, m. p. 343—344°) is suspended in glacial acetic acid and reduced by stannous chloride and 23% hydrochloric acid below 60°; by the addition of sodium acetate and acetic anhydride, the product of reduction is isolated as 6-nitro-4-acetylaminoresorcinol, m. p. 261° (decomp.), which is hydrolysed by concentrated hydrochloric acid, yielding the *hydrochloride*, m. p. above 300°, of 6-nitro-4-aminoresorcinol, m. p. 160—161° (decomp.). The reduction of 4 : 6-dinitroresorcinol by tin and hydrochloric acid and the treatment of the product with acetic anhydride yield 4 : 6-diacetylaminoresorcinol, m. p. 335° (decomp.), which forms a *dibenzoate*, m. p. 214°.

6-Nitro-4-nitrosoamino-3-hydroxy-o-benzoquinoneoxime,



obtained from aqueous 6-nitro-4-aminoresorcinol hydrochloride or

hydrobromide and sodium nitrite (2 mols.) at 0°, forms dark yellow, hexagonal plates, and explodes when heated. The substance is regarded as a nitrosoamine, and not as an *anti*-diazohydroxide, because it does not react with acetyl chloride or acetic anhydride, and its solution in alcoholic hydrogen chloride does not combine directly with alkaline β -naphthol; its solution in concentrated hydrochloric acid is very stable, and the diazonium salt thereby produced combines at once with alkaline β -naphthol, forming 6-nitro-3-hydroxy-1:2-quinoneoxime-4-azo- β -naphthol. The substance shows the character of a quinoneoxime, a 1% solution in dilute acetone dyeing chromed wool a tobacco-brown colour; in faintly alkaline β -naphthol solution, the dyed wool acquires a distinct blue tinge. When the nitrosoamine in concentrated hydrochloric acid is treated with copper powder in the cold, the hydrochloride, $C_6H_5O_2N_2Cl, HCl$, m. p. 204—205°, of 4-chloro-5-nitro-3-hydroxy-1:2-quinoneoxime, yellow needles, m. p. 155°, is obtained, a 1% solution of which produces a clearer and yellower tone on chromed wool than the nitrosoamine. C. S.

Preparation of Acetylchloroaminoanthraquinones. FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 224073).—Acetylchloroaminoanthraquinones, analogous to the phenyl compounds described by Bender (Abstr., 1887, 44), are readily obtained by the action of hypochlorous acid on an aqueous or dilute acetic acid solution or suspension of the required acetylaminanthraquinone; if glacial acetic acid is employed, nuclear substituted derivatives are formed.

Acetylchloro- β -aminoanthraquinone is prepared by heating the components together on the water-bath until a permanent yellow colour is obtained; it forms small needles, somewhat soluble in nitrobenzene.

Acetylchloro- α -aminoanthraquinone requires greater excess of hypochlorous acid and more prolonged heating for its preparation.

These compounds are initial substances in the preparation of dyes.

F. M. G. M.

Preparation of β -Anthraquinonylcarbimide from β -Aminoanthraquinone. FARBWERKE FORM. MEISTER, LUCIUS & BAFFING (D.R.-P. 224490).— *β -Anthraquinonylcarbimide*, m. p. 173°, is prepared by treating β -aminoanthraquinone with carbonyl chloride in nitrobenzene or xylene solution and keeping the mixture at the ordinary temperature until no red coloration is produced with dilute alcohol. The liquid is then heated to a temperature of 130—150°, when, on cooling, the product separates in colourless crystals. By treatment with moderately concentrated sulphuric acid, it is decomposed, yielding β -aminoanthraquinone with evolution of carbon dioxide.

F. M. G. M.

[Preparation of Aminoanthraquinone Thio-ethers.] FARBENFABRIKEN FORM. FRIEDRICH BAYER & Co. (D.R.-P. 224589).—An account of the preparation of dyes obtained by the action of aliphatic mercaptans on negatively substituted anthraquinone derivatives (containing either halogen, nitro- or sulphonic groups) in aqueous

alkaline solution. The following compounds are mentioned: 1-Amino-4-ethylthiolanthraquinone, bronze prisms; 1-benzoylamino-4-ethylthiolanthraquinone, bronze needles; 1-acetyl-amino-4-ethylthiolanthraquinone, red crystals; 1-amino-2:4-diethylthiolanthraquinone, red leaflets; 1:5-diamino-4:8-diethylthiolanthraquinone, steel-blue leaflets; sodium 1-ethylthiolanthraquinone-5-sulphonate, orange leaflets; 1:5-diethylthiolanthraquinone, yellow leaflets; sodium 1:4-diethylthiolanthraquinone-8-sulphonate, red needles.

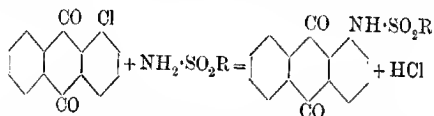
The colour of the solutions of these substances in various solvents is tabulated in the patent.

F. M. G. M.

[Preparation of Benzoylaminoanthraquinones.] FARNEN-FABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 225232).—A tabulated list of substituted benzoylamino- and dibenzoyldiamino-anthraquinones and their condensation products, with the colours of their solutions in pyridine, concentrated sulphuric acid, when dyed on wool, and in the vat.

F. M. G. M.

Preparation of Arylsulphonaminoanthraquinones. FRITZ ULLMANN (D.R.-P. 224982).—When substituted halogen anthraquinones are heated with arylsulphonamides and potassium carbonate in the presence of copper acetate in boiling nitrobenzene solution (or, if necessary, at higher temperatures), the following reaction takes place:



1-*p*-Toluenesulphonaminoanthraquinone, long, yellow needles, m. p. 225°, was obtained from 1-chloroanthraquinone and *p*-toluenesulphonamide.

2-Iodoanthraquinone, needles, m. p. 170°, is prepared by the method described for 1-iodo-2-methylantraquinone (Scholl, Abstr., 1907, i, 540), and when treated as above yielded 2-*p*-toluenesulphonaminoanthraquinone; this forms yellow needles.

1:2-Anthraquinonylsulphonaminoanthraquinone, prepared from 1-chloroanthraquinone and anthraquinone-2-sulphonamide, is insoluble in the ordinary organic solvents, but dissolves in concentrated sulphuric acid, yielding a red solution.

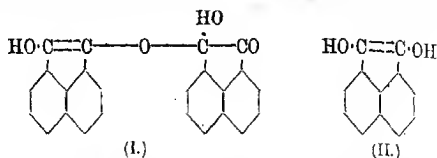
1:5-Dibenzenesulphonyldiaminoanthraquinone, a yellow, crystalline powder, was obtained from 1:5-dichloroanthraquinone and benzenesulphonamide.

F. M. G. M.

Preparation of Reduction Products of Acenaphthenequinones. KALLE & Co. (D.R.-P. 224979).—Reduction products from acenaphthenequinones have previously been studied; it is found that less energetic reduction, or the employment of milder reducing agents, gives rise to different products.

The compound (probably I) is produced by the action of alkaline

reducing agents; it forms yellow prisms, m. p. 248°, may be crystallised from tetrachloroethane, and yields a *hydrogen sulphite* and an *acetyl*



derivative on treatment respectively with sodium hydrogen sulphite or acetic acid. The second compound (probably II) is obtained with acid, neutral, or alkaline reducing agents; it crystallises from alcohol in needles, has m. p. 254°, and forms two series of salts which are soluble in water. One alkali salt is pale blue, the other (when excess of alkali is employed) a deep violet blue; the *magnesium* salts are colourless. This substance can be acetylated, and combines with sodium hydrogen sulphite and with hydroxythionaphthens to form vat dyes.

F. M. G. M.

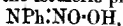
Preparation of Anthraquinone Derivatives. KINZLEBERGER & Co. (D.R.P. 223210).—When anthraquinone is heated at 160° with sodium hydroxide and zinc dust (or other alkaline reducing agents) it yields a *dianthranol*, $\text{C}_{18}\text{H}_{18}\text{O}_2$, m. p. 230°. This on oxidation with alkaline potassium permanganate gives a compound, $\text{C}_{18}\text{H}_{16}\text{O}_2 = \text{CO} < \text{C}_6\text{H}_4 > \text{C}:\text{C} < \text{C}_6\text{H}_4 > \text{CO}$, forming yellow crystals, which turn green on pressure and blacken at 300° without fusion.

F. M. G. M.

Behaviour of Some Derivatives of Phenylhydroxylamine. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 122–129).—Additional reasons are adduced for the formula assigned (this vol., i, 552) to the product of the action of nitro-benzene on safrole, which is identical with that obtained by the action of phenylhydroxylamine on methylenedioxy-cinnamaldehyde. The double linking between carbon atoms appears to be connected with the fact that the substance is coloured, since the analogous derivatives of benzaldehyde and phenylacetaldehyde are white. Moreover, β -cyclocitral yields a colourless derivative, so that the double linking in the above compound is probably in the side-chain. Benzoylacetalddehyde also yields a yellow derivative, although the constitution of the latter is not quite clear.

The *N*-phenyloximes described yield with hydroxylamine the corresponding oxime and phenylhydroxylamine, and they are rapidly affected by light. The action of light has been investigated further in the case of some analogous compounds. The cinnamaldehyde derivative, when exposed to light in sealed tubes freed from air, yields cinnamaldehyde and cinnamylideneaniline, $\text{CHPh}:\text{CH}:\text{CH}:\text{NPh}$. At the same time small quantities of other substances are formed, and an odour of isonitrile is perceptible. The benzaldehyde derivative, when

exposed to sunlight and air, forms benzaldehyde, nitrosobenzene, and benzanilide (compare Ciamician and Silber, *Abstr.*, 1905, i, 335), in addition to small quantities of *o*-oxybenzene, *o*-hydroxyazobenzene, and dibenzaniline. Nitrosophenylhydroxylamine, $\text{O:NPh:N}\cdot\text{OH}$, should form diazobenzene hydroxide analogously, and, in fact, an alkaline solution of it containing α -naphthol deposits benzeneazonaphthol when exposed to light. The process is rapid enough to have application in photography. The salts of the isomeric phenylnitroamines,



are acted on similarly, but more slowly. The sodium derivative of nitrosophenylhydroxylamine yields nitrosobenzene rapidly in the light. Unsaturated nitro-derivatives, such as 7-nitrostilbene and piperonalnitroethane, are also decomposed by light.

When β -cyclocitral and phenylhydroxylamine are kept in a sealed tube in the dark for some days, *N*-phenyl- β -cyclocitraloxime, $\text{C}_{16}\text{H}_{21}\text{ON}$, is formed. It forms long, colourless needles, m. p. 109–110°. It is acted on by permanganate, nitrosobenzene being formed, and it is rapidly hydrolysed by dilute sulphuric acid. When it is exposed to light, it quickly resinifies, an odour of cyclocitral and isonitrile is observed, and nitrosobenzene is formed. The last-named substance can be recognised by means of test-papers impregnated with hydroxylamine hydrochloride, sodium carbonate, and α -naphthol. β -cyclocitraloxime, $\text{C}_{13}\text{H}_{17}\text{ON}$, prepared by the action of hydroxylamine on the above ether, or on β -cyclocitral, forms large, colourless rhomboidal crystals, m. p. 84°, has a characteristic odour, is volatile in steam, and is readily hydrolysed by acids. β -cyclocitralsemicarbazone, $\text{C}_{11}\text{H}_{19}\text{ON}_2$, forms a felted mass of colourless needles, m. p. 209° (decomp.); Tiemann (*Abstr.*, 1901, i, 158, 599) describes a semicarbazone, m. p. 166–167°. By the action of phenylhydroxylamine on benzoylacetalddehyde, a substance, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$, is obtained, crystallising in orange needles, m. p. 158° (decomp.), which when warmed with permanganate yields nitrosobenzene, but is stable towards light.

R. V. S.

Nerol and Thymol in French Lavender Oil. F. ELZE (*Chem. Zeit.*, 1910, 34, 1029).—From a French lavender oil, having D_{20}^{25} 0.889, n_D^{20} 1.4620, and saponification number 99, a portion boiling at 85–100°/5 mm. was separated by distillation under reduced pressure. From this thymol was obtained by extraction with a dilute solution of sodium hydroxide, and from the residue nerol was isolated as the acid phthalate.

T. A. H.

Molecular Rearrangements in the Camphor Series. III. Oxidation Products of *l*- and *d*-Lauroleone. WILLIAM A. NOYES and C. G. DERRICK (*J. Amer. Chem. Soc.*, 1910, 32, 1061–1064. Compare *Abstr.*, 1909, i, 133, 560).—Contrary to the authors' previous statements, the diketone obtained by oxidising *l*-lauroleone does not undergo condensation readily. It has b. p. 204°/750 mm. (corr.); the optical activity varies with the method of preparation. The *disemicarbazone* has m. p. 194° (corr.), but the *dioxime* and *phenylhydrazone* are oily.

The rotation of *d*-lauroleone varies with the method of preparation; a specimen prepared by the action of sodium nitrite on the hydro-

obloride of aminolauroic acid had $[\alpha]_D^{25}$ 28.15°, whilst the density and b. p. were identical with that of the *l*-form. Oxidation with cold alkaline permanganate gave a diketone, $C_8H_{14}O_2$; the diisemicarbazone, after melting at 192° (corr.), solidified, and then had m. p. 225° (corr.).

The properties of the oxidation products of laurolene are in accord with Eykman's representation of the structure of this substance (Abstr., 1907, i, 378). W. O. W.

Molecular Rearrangements in the Camphor Series. IV. Synthesis of Laurolene. WILLIAM A. NOYES and L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1910, 32, 1064—1068. Compare preceding abstract).—The dimethylcyclopentanone obtained by heating *d-ad*-dimethyladipic acid with lime is optically inactive. Grignard's reaction was applied to convert the product into 1:2:3-trimethylcyclopentanol, $C_8H_{16}O$, a liquid having b. p. 56—60°/8 mm., D_4^{20} 0.9121, n_D^{20} 1.4554. This substance loses water when heated, and is converted into laurolene; the transformation, however, is more easily effected by Zelinsky's method (Abstr., 1902, i, 2). The hydrocarbon thus prepared has h. p. 120—122°, n_D^{20} 1.4461, and on oxidation furnishes a diketone identical with that obtained from aminolauroic acid. The refractive index of synthetic laurolene is slightly less than that of the natural product, possibly through the presence of some ψ -laurolene.

The structure of laurolene as Δ^1 -1:2:3-trimethylcyclopentene is, therefore, fully established. W. O. W.

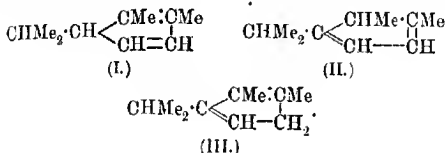
Molecular Rearrangements in the Camphor Series. V. Mechanism of the Reactions by which Laurolene is Formed. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1910, 32, 1068—1070. Compare preceding abstracts).—A theoretical discussion. A methyl group is assumed to become detached and to unite with an adjacent carbon atom in the formation of laurolene from camphanic acid (Crossley and Renouf, *Trans.*, 1906, 89, 27) and from aminolauroic acid or anhydride. W. O. W.

Some Thujene Derivatives. IWAN L. KONDAKOFF and W. SKWORZOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 497—504. Compare Abstr., 1904, i, 438).—The authors consider that the structure of the compounds in the thujene series has not yet been satisfactorily settled. Thujene has never yet been obtained in a pure state, the product consisting of a mixture of dicyclic thujenes together with terpene and some other hydrocarbon. When the thujene obtained by the xanthate method is treated several times with 1% potassium permanganate, a tricyclic hydrocarbon or some stereoisomeric thujene was obtained, having b. p. 147.5—149.5°, D_4^{20} 0.8220, n_D^{20} 1.44809, $[\alpha]_D^{20}$ +109.09°.

By removing hydrogen bromide from thujyl bromide, an unsaturated alcohol was obtained, b. p. 218—221°/760 mm., 96—100°/10 mm., D_4^{20} 0.9174, n_D^{20} 1.47936, $[\alpha]_D^{20}$ +13.22°. Similarly, from the chloride, the alcohol obtained has b. p. 205—208°, D_4^{20} 0.8947, n_D^{20} 1.46123, $[\alpha]_D^{20}$ +23.22°. The taste and odour of both alcohols are alike, and similar to that of menthol and terpineol. They do not yield urethanes, are largely converted into resins by the action of hydrochloric acid and

of succinic anhydride at 150° , are readily oxidised by concentrated potassium permanganate, and readily lose water. They are probably tertiary alcohols containing a five-membered ring, and are very similar to the alcohol obtained by Semmler from sabinene (Abstr., 1907, i, 145), excepting that in the latter the double bond is in the side-chain, whereas in the former it occurs in the ring.

By the action of hydrochloric acid on isothujene, and also on the alcohol described above, a *dihydrochloride*, $C_{10}H_{18}Cl_2$, b. p. $121.5-125.5^{\circ}/16$ mm., D^{20}_D 1.0697, n_D 1.48458, $[\alpha]_D +1.86^{\circ}$, is obtained, together with resinised products. When treated with sodium acetate, a *hydrocarbon*, $C_{10}H_{18}$, b. p. $176-180^{\circ}$, D^{18}_D 0.8540, n_D 1.47586, $[\alpha]_D +3.11^{\circ}$, was obtained, the constitution of which may be (II) or (III) if formula (I) is taken as that of isothujene.



Z. K.

Essential Oils. ROURE-BERTRAND FILS (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1910, [iii], 1, 34-62).—[JUSTIN DUPONT and LOUIS LABAUNE.]—It has been shown previously that when cinnamyl alcohol in toluene is treated with hydrogen chloride at 100° , a chloride, C_9H_9Cl ,

is formed (this vol., i, 185). This is now shown to be cinnamyl chloride. On treatment with silver nitrate in alcohol, it yields a mixture of products, from which, by the action of sodium and subsequent fractional distillation, α -phenylallyl ethyl ether and cinnamyl ethyl ether were isolated. In addition, the mixture contains α -phenylallyl alcohol and cinnamyl alcohol (compare Charon, *Bull. Soc. chim.*, 1910, [iv], 7, 86). A good yield of the supposed linalyl chloride described already may be obtained by treating either linalool or geraniol in dry benzene with phosphorus trichloride (this vol., i, 184).

Hydrogen bromide reacts with geraniol or with *l*- or *d*-linalool, dissolved in toluene and maintained at 100° , to form a *bromide*, D^{15}_D 1.4450, $n_D \pm 0$, n_D^{15} 1.507, b. p. $102-103^{\circ}/6$ mm., and this, when treated with potassium acetate in presence of toluene, yields linalyl acetate. When the bromide is treated with sodium ethoxide, it yields geranyl ethyl ether, b. p. 218° ; with silver hydroxide, it gives linalool, and with silver nitrate, it furnishes linalol, geranyl ethyl ether, and possibly linalyl ethyl ether. In view of this complex reaction with silver nitrate, it is difficult to assign a constitutional formula to the bromide or the corresponding chloride.

Orange flowers collected in May and in October, 1909, yielded, by extraction with light petroleum, 736.3 and 663.6 grams respectively of total essential oil per 1000 kilos. of flowers. The May oil had D^{15}_D 0.8899, n_D^{15} 1.478, $n_D = -0.48$, acid value 0.7, saponification value 2.2, esters 24.6%, alcohols 51.0%, methyl anthranilate 3.53%. The

autumn oil had D^{15}_D 0.8887, n^{20}_D 1.476, $\alpha_D = -4.6'$, acid value 1.0, saponification value 95.8, esters 33.4%, alcohols 57.0%, methyl anthranilate 2.74%. These extracted oils differ from oil of neroli (distilled oil) in being levorotatory, indicating that a change in rotation occurs as the result of distillation in steam. The higher yield of oil in May and the greater richness of this oil in methyl anthranilate is probably due to more active metabolism in the plant at that period and to the warmer temperature. Extracted orange flower oil usually contains over 7.0% of methyl anthranilate, and the low yield in these two samples may have been a result of the severe winter preceding the orange flower harvest of 1909. Analyses of the two oils, after removal of methyl anthranilate by Hesse and Zeitschel's process (Abstr., 1901, ii, 209), gave constants indicating that the May oil was poorer in combined and total alcohols than the October oil, the quantity of free alcohols being about the same; similarly, the October oil was richer in the primary alcohols, geraniol and nerol. It seems likely, therefore, that in May the flowers draw their supply of oil from the young branches, and in October from the older branches. The results also afford a further proof of the formation of terpene compounds in green organs.

Myrica Gale yielded, by steam distillation, 0.0443% of a greenish-yellow, volatile oil, having D^{25}_D 0.8984, $\alpha^{20}_D = -5.16'$, acid value 3.48, saponification value 17.98, esters 5.1%, total alcohols 14.4%, and free alcohols 10.5%. The oil exhibited a powerful purgative action, as did also a resin contained in the plant.

Java patchouli leaves furnished 0.803% of oil having D^{15}_D 0.9564, $\alpha_D = -28.8'$, saponification value 6.3, saponification value of acetylated oil 40.4.

Oil of *Mentha arvensis* var. *Javanica* had D^{15}_D 0.9979, $\alpha_D = +0.94'$, acid value 69.8, saponification value 49.7, saponification value after acetylation 153.3, corresponding with esters 17.5%, total menthol 48.2%, free menthol 34.4%, ketones or aldehydes, traces or none. The oil did not deposit crystals at -15° .

Ylang-ylang oil from Mayotte had D^{15}_D 0.9324, $\alpha_D = -47.40'$, acid value 1.0, saponification value 113.4, corresponding with esters 39.7%, total alcohols 41.0%, and free alcohols 3.8%.

An oil from French Guiana had D^{15}_D 0.8864, $\alpha_D = 0.2'$, total alcohols 71.3%, esters 5.8%, and dissolved to the extent of 80% in sodium hydrogen sulphite solution. The oil had a lemon-like odour, and was described as derived from *Andropogon Nardus*, L. The results indicated that it was derived from *A. citratus*, De Cand., and was abnormally rich in citronellal and geraniol.

In continuation of previous work (this vol., i, 401), Delépine finds that samphire oil contains dipentene, not limonene; in addition to the constituents already described, the oil contains traces of two phenols (one crystalline, and the other possessing an odour of cresote), and a small quantity of an alcohol having an odour of roses, with other indefinite products.

T. A. H.

Essential Oils. SCHIMMEL & Co. (Bericht, October, 1910).—The fruits of *Pimenta acris* from Mauritius yielded 3.3% of bright brown

oil, D^{15} 0.9893, $\alpha_D -1^{\circ}20'$, n_D^{20} 1.51902, eugenol 70% (compare *Bull. Imp. Inst.*, 1910, 8, 4).

Camphor oil from German East Africa had D^{15} 0.9203, $\alpha_D +39^{\circ}42'$, n_D^{20} 1.47753, and deposited camphor on cooling.

Cocking (*Chemist and Druggist*, 1910, 77, 19) has devised a method for detecting "Illurin balsam" in copaiba balsam, depending on the fact that if oil be distilled from these balsams in ten equal fractions, those from copaiba balsam show increasing laevorotation, whilst those from Illurin balsam show increasing dextrorotation.

Bergamot oil adulterated with ethyl citrate yields on evaporation to constant weight on the water-bath, a residue having a saponification value above that found for a similar residue from genuine oil, namely, 160, and the increase in the value may be used to obtain a rough indication of the extent of the adulteration. In the saponified product citric acid may be detected by means of calcium chloride or by Denigès' test (*Abstr.*, 1899, ii, 454), the acid being first converted into acetonedicarboxylic acid by means of lead dioxide. Genuine bergamot oil contains only traces of citric acid, which, however, can be detected by Denigès' reaction. Genuine bergamot oil shows the same saponification value after heating at 100° during thirty or sixty minutes with $N/2$ -potassium hydroxide in alcohol, but if terpinyl acetate is present the saponification value increases with longer heating, and in any case is higher than that shown by genuine oil. Glycerol acetate may be detected by Jeancard and Satie's method, which depends on the partial extraction of the glycerol acetate with water. For the detection and estimation of sophistication by esters of non-volatile acids, 1.5 to 2 grams of oil is treated in the ordinary way for the determination of the total saponification value [acid and ester values]. The saponified product is made distinctly alkaline, evaporated to dryness, the residue acidified with sulphuric acid, and the acid value of the distillate determined. The difference between the "total saponification value" and the "volatile acid value" for genuine oil is not more than 7. These methods are applicable also to lavender and "petit grain" oils.

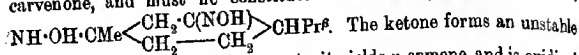
In Réunion geranium oil, linalool, α -terpineol, and phenylethyl alcohol were found in addition to traces of menthol and of an alcohol with an odour recalling that of borneol. Terpinenol may also be present.

Garlic contains according to Rindqvist (*Apoth. Zeit.*, 1910, 25, 105) a glucoside, *allin*, which is decomposed by a specific enzyme, *allisin*, yielding garlic oil and laevulose.

A Chinese peppermint oil had D^{15} 0.9187, $\alpha_D -44^{\circ}2'$, ester value 43.9, total menthol 64.0%, and was soluble in 2.5 or more volumes of 70% alcohol.

Japanese peppermint oil contains Δ^1 -menthenone, b. p. 235–237°/752 mm., D^{15} 0.9382, D^{20} 0.9343, $\alpha_D +1^{\circ}30'$, n_D^{20} 1.48411 (compare Wallach, *Abstr.*, 1908, i, 812). The semicarbazone exists in the sparingly soluble α -form already described by Wallach (*loc. cit.*), and also in a readily soluble β -form, m. p. 171–172°. With hydroxylamine it forms an *oxime*, m. p. 107–109°, and an *oxamino oxime*, m. p. 164–165°, which closely resembles the corresponding derivative of

carvenone, and must be constituted in an analogous manner, thus:



dibromide. With dehydrating agents, it yields *p*-cymene, and is oxidised by ferric chloride to thymol. Phosphorus pentachloride converts it into monochloroterpinene, and this on reduction with sodium in alcohol yields α -terpinene. On oxidation with permanganate the ketone furnishes formic acid, α -hydroxy- α -methyl- δ -isopropyladipic acid, m. p. 143°, α -isopropyl- γ -acetylbutyric acid (the *semicarbazone* has m. p. 158—159°), and α -isopropylglutaric acid, the third acid resulting from further oxidation of the second, and the fourth in like manner from the third. These reactions can best be explained by the formula assigned to the ketone by Wallach (*loc. cit.*). For the characterisation of the ketone in essential oils, it is best isolated as the compound with sodium hydrogen sulphite, and identified by means of the α -semicarbazone. According to Murayama, Japanese peppermint oil also contains *l*-limonene (*J. Pharm. Chim.*, 1910, [vii], 1, 549).

A sage oil from Cyprus had D_{20}^{25} 0.9263, n_D^{20} 1.46664, acid value 0, ester value 6.4, and acetyl ester value 36.0, and resembles Corfu sage oil.

From the first runnings of the distillation of sandalwood, the following constituents not previously observed have been isolated: (1) Santenone, $C_{15}H_{24}O$, m. p. 58—61°, b. p. 193—195°, n_D^{20} 1.4449 in alcohol, is identical with the ketone prepared by Aschan (Abstr., 1908, i, 94) and by Semmler, and named by the latter π -norcamphor (Abstr., 1907, i, 1062); it yields a liquid *oxime*, b. p. 110—113°/6 mm., from which the ketone is not regenerated by warming with acids. (2) "Santenone alcohol," $C_{15}H_{26}O$, m. p. 58—62°, b. p. 196—198°, is apparently identical with Semmler's π -norisoborneol (*loc. cit.*); on oxidation it yields santenone (π -norcamphor), furnishes a liquid *phenylurethane*, and is not etherified when warmed with alcohol and sulphuric acid. The isomeric alcohol (Aschan's santenol, *loc. cit.*; Semmler's π -norborneol, *loc. cit.*) on the contrary is etherified under these conditions, and yields, for example, *santenyl methyl ether*, $C_{16}H_{28}O$, b. p. 177—179°, D_{20}^{25} 0.9251, n_D^{20} 1.45841. It is suggested that Semmler's π -norborneol (Aschan's santenol) should now be called *isosantenol* and his π -norisoborneol should be named *santenol*. (3) A *hydrocarbon*, $C_{11}H_{18}$, b. p. 183°, D_{20}^{25} 0.9133, D_{20}^{20} 0.9092, n_D^{20} 1.47860, which may prove to be identical with Semmler's *nortricycloeksantalane* (Abstr., 1907, i, 432), since the latter, in view of Semmler's more recent work, must have the formula $C_{11}H_{18}$. (4) *Nortricycloeksantalal*, $C_{11}H_{16}O$, b. p. 86—87°/6 mm., 222—224°/761 mm., D_{20}^{20} 0.9938, n_D^{20} 1.48393, is identical with Semmler's product (this vol., i, 573). It yields a liquid *oxime*, b. p. 135—137°/7 mm., and on oxidation by air in dilute alkali furnishes the corresponding *acid*, m. p. 91—93°, n_D^{20} 1.3317 (in alcohol). On oxidation with permanganate, *teresantalic acid* is formed. The aldehyde can also be obtained from normal sandalwood oil. (5) *Teresantalol*, $C_{10}H_{16}O$, m. p. 112—114°, identical with Semmler and Bartlett's product (Abstr., 1907, i, 703) prepared from *teresantalic acid*. (6) *isoValeraldehyde*.

Müller's santalone (Abstr., 1900, i, 678) was isolated by means of the semicarbazone. It occurs associated with an isomeric ketone, yielding a semicarbazone, m. p. 208—209°, and an oxime, m. p. 100° (approx.). The sesquiterpene portion of the oil was separated by fractional distillation into α -santalene, b. p. 118°/7 mm., 252°/753 mm., D^{15}_D 0.9132, n_D^{20} -3°34', n_D^{20} 1.49205, and β -santalene, b. p. 125—126°/7 mm., D^{20}_D 0.8940, n_D^{20} -41°3', n_D^{20} 1.49460 (compare Semmler, Abstr., 1907, i, 781). It is probable that pure α -santalene is slightly dextrorotatory. On hydration, α -santalene furnishes a tertiary alcohol, $C_{15}H_{26}O$, b. p. 154—157°/5—6 mm., D^{15}_D 0.9787, D^{20}_D 0.9753, n_D^{20} 1.51725, which has a cedar-like odour, and on treatment with formic acid loses water. The portion of the hydrocarbon recovered from the hydration process is different from the original material (compare von Soden and Müller, Abstr., 1899, i, 924).

Brassica juncea seed from India yielded an oil having D^{15}_D 0.9950, n_D^{20} +0°13', n_D^{20} 1.51849, and soluble in 10 vols. of 70% alcohol. It boiled for the most part between 150—160° and 174—178°. The principal constituents were dimethyl sulphide, allyl cyanide, allylthiocarbimide (40%), and a crotonylthiocarbimide (50%), b. p. 175—176°, D^{15}_D 0.994, n_D^{20} +0°3', n_D^{20} 1.52398, which furnished a thiocarbimide, m. p. 69—70°.

Juniper berry oil contains camphene (compare Abstr., 1909, i, 818).

Chamaecyparis Lawsoniana furnished 1% of citron-yellow oil, D^{15}_D 0.9308, n_D^{20} +23°48', n_D^{20} 1.48844, acid value 3.7, ester value 61.6, acetyl ester value 78.8, containing some decaldehyde (?).

The leaves of *Cinnamomum glanduliferum* contained *d*-camphor. *Dacrydium Franklinii* wood yielded an oil, D^{15}_D 1.0443, n_D^{20} +0°6', n_D^{20} 1.53287, containing much methyleugenol with some eugenol.

Eugenia apiculata leaves furnished 1.27% of brown oil, D^{15}_D 0.892, n_D^{20} +12°40', n_D^{20} 1.47821, acid value 5.5, ester value 25.8, and acetyl ester value 65.3.

Perilla nankinensis leaf oil, D^{15}_D 0.9265, n_D^{20} -90°, n_D^{20} 1.49835, contains an aldehyde, b. p. 91°/4.5 mm., 104°/9 mm., 235—237°/750 mm., D^{20}_D 0.9645, D^{15}_D 0.9685, $[\alpha]_D^{20}$ -150.7°, n_D^{20} 1.50693, which yields an oxime, m. p. 102°, and a phenylhydrazone, m. p. 107.5°. The corresponding acid has m. p. 130°, and forms scaly crystals. A dextro-modification of the same aldehyde has been found in a "false camphor wood."

Thymbra spicata herb from Smyrna gave 1.5% of oil having an odour of thyme and containing 66% carvacrol. It had D^{15}_D 0.9460, n_D^{20} 0°, n_D^{20} 1.50675.

Xanthoxylum alatum fruits gave 3.7% citron-yellow oil, D^{15}_D 0.8653, n_D^{20} -23°35', n_D^{20} 1.48131, and 0.9% of a crystalline, odourless substance, m. p. 83°, from which a small yield of a benzoyl derivative, m. p. 89°, was obtained. The oil appeared to consist mainly of hydrocarbons, and its odour recalled that of phellandrene.

Alpinia galanga oil is lemon-yellow, possesses a pungent, aromatic odour, and shows the following constants: D^{15}_D 0.9847, n_D^{20} +4°20', n_D^{20} 1.51638, and contains, according to Ullée, pinene, cineol, camphor, and methyl cinnamate.

Gastrochilus pandurata oil resembles estragon and basil oils in odour,

and has D^{15}_D 0.8746, $\alpha_D + 10.24'$, n_D^{20} 1.48957, ester value 17.3, and is incompletely soluble in 10 vols. of 80% alcohol.

A résumé of recent work on the botany, pharmacology, analysis, and chemistry of essential oils is also given.

T. A. H.

Cerebron. IV. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1910, 68, 464—470. Compare Abstr., 1907, i, 168).—Details are given of the preparation of cerebron from ox-brain, and the analysis of various fractions separated by extracting agents. The purest fraction was obtained in crystalline form, and contains C 69.19%, H 11.35%, and N 1.7%. The m. p. is 212—213°. Further work is promised on a second galactoside with which cerebron is usually mixed.

W. D. H.

Effect of Alkali on Melanin. ROSS AIKEN GORTNER (*J. Biol. Chem.*, 1910, 8, 341—363).—Alkali in small concentration readily destroys the greater portion of the melanin molecule, the nitrogen falling specially, whilst the carbon and oxygen percentages increase; the sulphur remains practically constant. If the concentration of alkali does not exceed 0.2%, a melanin is extracted from black wool, which is of constant composition, contains no ash, and is readily soluble in acids.

W. D. H.

Synergisin, the Prochromogen of the Respiration Pigment of Wheat Germs. WLADIMIR PALLADIN (*Biochem. Zeitsch.*, 1910, 27, 442—449).—The prochromogen of wheat, *synergisin*, is decomposed by emulsin with production of a chromogen which is oxidised by peroxylase without addition of hydrogen peroxide. The prochromogen is extracted by ethyl and methyl alcohol, and is precipitated by acetone. It is not soluble in ether.

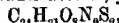
Taka-diastase, like emulsin, decomposes synergisin with production of a chromogen which is oxidised by peroxylase. Pepsin is without action.

A number of substances were treated with emulsin and peroxylase in order to ascertain whether pigments are produced. Arbutin yielded a red coloration, less intense than that obtained with the chromogen from wheat, whilst the following compounds gave negative results: aesculetin, amygdalin, apiin, cholesterol, crategin, cyclamin, digitalin, filicin, galactose, inositol, lecithin, phytin, quercitrin, raffinose, salicin, saligenin, solanine, syringin, and tyrosine.

Synergisin is a phosphatide containing a carbohydrate group.

N. H. J. M.

Compounds of Acid Dyes with Various Organic Bases. LEOPOLD RADLBERGER (*Zeitsch. physiol. Chem.*, 1910, 68, 391—394. Compare Abstr., 1908, i, 1001).—By mixing hot aqueous solutions of the components and cooling, the following insoluble or sparingly soluble salts have been obtained. Biguanide sulphate (which crystallises in large plates or in slender needles) yields the salt,



with orange II, and $C_{24}H_{23}O_7N_{12}S_2$ with crystal-ponceau. Acetyl-

guanamine acetate yields an orange salt, $C_{20}H_{19}O_4N_7S_2H_2O$ (very hygroscopic when anhydrous), with orange II. C. S.

Causes of the Coloration of Animal Fibres. II. WILHELM SCIDA (*Zeitsch. physiol. Chem.*, 1910, 68, 381—390. Compare Abstr., 1907, ii, 112).—Having shown that aqueous guanidine hydrochloride yields with picric acid and with crystal-ponceau sparingly soluble, crystalline precipitates, the filtrate containing in the first case all, in the latter 94.2%, of the chlorine, the author uses a reagent prepared by dissolving 5 grams of guanidine hydrochloride and 3 grams of acetic acid in 100 c.c. of water to test the acidity or basicity of a series of dyes which do not give in aqueous solution precipitates with acids alone. The results are: (i) all purely basic, non-sulphonated dyes do not give precipitates; (ii) in dyes which are aminosulphonic acids a decrease of precipitability frequently accompanies an increase in the number of amino- and of sulphy-groups; the generalisation, however, is not always trustworthy; (iii) nearly all of the hydroxyazo-dyes examined (with the exception of eosamine-B and azomagenta G), and also picric acid and alizarin-red, are more or less quantitatively precipitated, the quantitative course of the reaction being influenced by the number and the position of the hydroxyl and the sulphy-groups; (iv) the precipitation of hydroxy-dyes containing free or alkylated amino-groups is less the greater the number of amino-groups present; (v) whilst tartrazine does not give a precipitate, dyes containing hydroxyl and carboxyl groups, or these and sulphy-groups, give precipitates whether amino-groups are present or not; however, dyes which contain amino- (or alkylated amino-) and carboxyl, but no hydroxyl, groups do not yield precipitates. The outstanding result of the experiments is the important rôle played in the fixing of acid dyes by basic substances, by phenolic hydroxyl and aromatic amino-groups, the carboxyl and sulphy-groups exerting a quite subordinate influence.

Having shown that preliminary treatment of animal fibres with phosphotungstic acid retards the fixation of acidic dyes (*Zeitsch. angew. Chem.*, 1909, 22, 2131), the author has examined the behaviour of the acid towards salts of guanidine. Any soluble salt of guanidine yields with phosphotungstic acid a white precipitate, which is easily soluble in ammonium hydroxide or carbonate; the precipitate remains colourless when boiled with a solution of an acidic dye, but instantly becomes coloured by the addition of a little ammonium hydroxide or carbonate, consequently experiments on guanidine in test-tubes follow quite the same course as those previously performed on animal fibres (*loc. cit.*). Since phosphotungstic acid is an excellent precipitant for the basic fission products of albumins, and since these products frequently contain the group NCN present in guanidine, there can be little doubt that the fixation of acidic dyes by albumins is due to these fission products or the NCN group contained therein; moreover, the chemical compounds formed by acidic dyes with animal fibres are probably constituted in stoichiometric proportions, since Radlberger has shown (Abstr., 1908, i, 1901) that the compounds of guanidine with acidic dyes are thus constituted.

An examination has been made of the behaviour of dyes towards

many substances related to the albumins or their fission products. The results are: (i) all aliphatic or cyclic substances containing the group $\text{N}\cdot\text{CO}\cdot\text{N}\cdot$ or $\text{N}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot$, such as carbamide, biuret, cyanuric acid, barbituric acid, alloxan, uric acid, theobromine, caffeine, phenyl-carbamide, α -phenylhydantoin, glycine anhydride, phenylglycine anhydride, do not yield precipitates with acidic dyes; some of them possessing acidic character (barbituric acid, uric acid, cyanuric acid, ammeline, ammeline) form sparingly soluble compounds with basic dyes; (ii) all derivatives of guanidine with open chains which do not contain substituent acidic groups (aminoguanidine, dicyanodiamide, guanylcarbamide, higuamide, arginine) form sparingly soluble compounds with acidic dyes; (iii) all cyclic compounds containing the guanyl group give sparingly soluble or insoluble compounds with acidic dyes. It is noteworthy that most of the preceding substances which form insoluble or sparingly soluble compounds with acidic dyes are also precipitated by phosphotungstic acid. C. S.

Molecular Weight of Tannin. LEO F. ILJIN (*J. pr. Chem.*, 1910, [ii], 82, 422—424).—The molecular weight of tannin, purified by the author's processes (*Abstr.*, 1909, i, 503), has been determined by the ebullioscopic method in acetone in MacCoy's modification of Landsberger's apparatus; the values, varying between 1247 and 1637, confirm those of Sahanéeff and of Walden. The author is of opinion that crude tannin contains, in addition to digallic acid and Nierenstein's leucotannin, a not inconsiderable quantity of a complex derivative of gallic acid, for which the name "tannin" should be reserved. C. S.

δ -Hydroxymethylfurfuraldehyde as the Cause of Some Colour Reactions of Hexoses. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Ber.*, 1910, 43, 2355—2361. Compare *Abstr.*, 1909, i, 288; this vol., i, 461).—The compound previously described as β -hydroxy- δ -methylfurfuraldehyde is now shown to be the ω -hydroxy-compound, $\text{O} \begin{array}{c} \text{C}(\text{CHO})=\text{CH} \\ \diagdown \\ \text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{CH} \end{array}$ as it can be obtained readily from chitose (Fischer and Andreae, *Abstr.*, 1903, i, 678), and when oxidised yields hydroxymethylpyromucic acid, $\text{O} \begin{array}{c} \text{C}(\text{CO}_2\text{H})=\text{CH} \\ \diagdown \\ \text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{CH} \end{array}$ (compare Kiermayer, *Abstr.*, 1896, i, 144), identical with the acid prepared by Fischer and Andreae (*loc. cit.*) and by Fenton and Gostling (*Trans.*, 1899, 75, 429). J. J. S.

ω -Hydroxymethylfurfuraldehyde and its Relationship to Cellulose. ERNST ERDMANN (*Ber.*, 1910, 43, 2391—2398).— ω -Hydroxymethylfurfuraldehyde (compare Alberda van Ekenstein and Blanksma, preceding abstract) can be prepared from Fenton and Blanksma, preceding abstract) can be prepared from Fenton and Gostling's crude ω -bromomethylfurfuraldehyde (*Trans.*, 1901, 79, 361, 807) by shaking with aqueous alcoholic silver acetate and extracting with ether. It has b. p. $72^\circ/0\cdot002$ mm., and the yield is 5.5 grams from 150 grams of filter paper. It has a pleasant odour, D_4^{20} 1.1022, and gives the usual aldehyde reactions. Its semioxazurone, $\text{C}_8\text{H}_9\text{O}_4\text{N}$,

forms colourless needles, m. p. 216°. When heated under pressure with oxalic acid solution at 134°, it yields an oil from which a *phenylhydrazone*, m. p. 137°, has been isolated. The same phenylhydrazone can be obtained from the oil, b. p. 110°/0.002 mm., formed as a by-product in the preparation of the ω -hydroxymethyl compound. It is suggested that this oil, h. p. 110°/0.002 mm., is identical with the product obtained by Kiermayer from sucrose (Abstr., 1896, i, 144). Its semioxazone is not molten at 260°.

J. J. S.

Action of Methyl Sulphate on Dimethylpyrone. ADOLF VON BAEYER (*Ber.*, 1910, 43, 2337—2343).—Kehrmann and Duttonhöfer's dimethylpyrone methiodide (Abstr., 1906, i, 447) is shown to have the formula $\text{I} \cdot \text{O} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} > \text{C} \cdot \text{OMe}$.

The parent substance, $\text{I} \cdot \text{O} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} > \text{CH}$, is termed pyroxonium iodide.

Dimethyl-p-methoxypyroxonium perchlorate, $\text{OMe} \cdot \text{C}_5\text{H}_2\text{Me}_2\text{O} \cdot \text{ClO}_4$, is obtained when dimethylpyrone and methyl sulphate are heated at 50° until the mixture becomes orange-coloured, and the cold product is treated with 20% perchloric acid solution. It is also formed by the action of perchloric acid solution on Kehrmann and Duttonhöfer's iodide. It crystallises from methyl alcohol, is sparingly soluble in cold water, and is resolved into its components when boiled with water for some time. An aqueous solution of ammonium carbonate converts the perchlorate or the iodide into 4-methoxylutidine, the picrate of which melts at 154°, and a solution of sodium acetate or water and magnesium carbonate react with the perchlorate, yielding the *methyl ether* of the enolic form of diacetylacetone, $\text{CH}_3\text{Ac} \cdot \text{C}(\text{OMe}) \cdot \text{CHAc}$, as a colourless oil.

J. J. S.

Preparation of Coumarin. FRITZ RASCHIG (D.R.-P. 223684).—The synthetical production of coumarin has been checked by the cost of the salicylaldehyde employed in the usual method of preparation; it is found that this can be replaced by an *o*-tolyl ester containing two atoms of chlorine in the side-chain.

Di-*o*-chlorotolyl phosphate (obtained by treating *o*-tolyl phosphate with chlorine at 160—180°) is mixed with anhydrous sodium acetate and heated at about 180° during six hours; the temperature is then raised to 220°, when pure coumarin distils and solidifies in the receiver. The phosphoric acid can be replaced by other acids.

F. M. G. M.

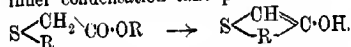
Constitution of α -Pyrocresol. FRANZ ZMERZLIKAR (*Monatsh.*, 1910, 31, 897—902. Compare Schwarz, Abstr., 1883, 204; Bott, *J.C.S.I.*, 1887, 6, 646; Bott and Miller, *Trans.*, 1889, 55, 51).—When α -pyrocresol oxide is fused with potassium hydroxide, the products are *m*-hydroxy-*p*-toluic acid ($\text{Me} : \text{OH} : \text{CO}_2\text{H} = 1 : 3 : 4$), *m*-hydroxyterephthalic acid, and *m*-cresol.

The formation of these compounds is readily accounted for on the assumption that α -pyrocresol oxide is 4:2'- or 4:4'-dimethylxanthone,

$\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3\text{Me}$; α -pyrocresol itself would then be the corresponding dimethylxanthan, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_3\text{Me}$. The identity of synthetical 4:4'-dimethylxanthone (Weber, Abstr., 1892, 1093) with α -pyrocresol oxide has been proved, and hence α -pyrocresol is 4:4'-dimethylxanthan. J. J. S.

Preparation of Phenoxozone. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 223367).—The preparation of phenoxozone, m. p. 118–119°, has previously been described (Ullmann and Stein, Abstr., 1906, i, 258); it is now found that it can be prepared in 74% yield by gradually heating sodium *o*-chlorophenoxide to 220° in an iron retort, and subsequently distilling under a pressure of 20–30 mm. F. M. G. M.

Preparation of Thionaphthen Derivatives from Arylthiolacetic Acids and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 224567).—When arylthiolacetic acids of the type $\text{R}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}'$ (where R is a simple or substituted benzene ring, or naphthalene residue, and R' hydrogen, a metal, alkyl, or aryl group) are treated with such reagents as phosphoric oxide, zinc, or aluminium chlorides, chlorosulphonic acid, or anhydrous oxalic acid, the following inner condensation takes place:



This reaction has only been studied previously with phenyl-, *o*- and *p*-tolyl-, and *p*-bromophenyl-thiolacetic acids, but has now been extended to naphthalene derivatives; the products when pure are colourless compounds soluble in alkali, and yielding vat dyes on oxidation.

2-Hydroxy-4-methylthionaphthen is prepared by heating ethyl *p*-tolylthiolacetate (obtained from thio-*p*-cresol and ethyl chloroacetate) with phosphoric oxide at 100–150°, and separating the product by distillation in steam; it forms long, colourless needles, m. p. 103°.

4-Chloro-2-hydroxythionaphthen, colourless needles, m. p. 100°, is similarly prepared from *p*-chlorophenylthiolacetic acid (m. p. 107°).

The compound, obtained from sodium α -naphthylthiolacetate, when treated with chlorosulphonic acid at 0–5° is yellow, and not volatile in steam. F. M. G. M.

Substituted Rhodanines and their Condensation Products with Aldehydes. IX. OSKAR ANTULICH (*Monatsh.*, 1910, 31, 891–895).—Ammonium *p*-anisylidenedithiocarbamate, prepared by Losanitsch's method (Abstr., 1907, i, 693), reacts with ethyl chloroacetate, yielding *p*-anisylrhodanine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{CS}\cdot\text{S} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, which crystallises from alcohol in yellow plates, m. p. 153°. The following condensation products have been obtained by the action of a glacial acetic acid solution of an aromatic aldehyde on the rhodanine.

1-*p*-Anisyl-3-benzylidenetherhodanine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{CS}\cdot\text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}\cdot\text{CHPh}$,

lemon-yellow prisms, m. p. 190°; 1-*p*-anisidyl-3-*m*-nitrobenzylidenes-rhodanine, $C_{17}H_{12}O_4N_2S_2$, a chrome-yellow, crystalline powder; 1-*p*-anisidyl-3-*p*-hydroxybenzylidenes-rhodanine, $C_{17}H_{13}O_4NS_2$, yellow needles from acetone, m. p. 258°; 1-*p*-anisidyl-3-*p*-dimethylaminobenzylidenes-rhodanine, $OMe \cdot C_6H_4 \cdot N \begin{smallmatrix} CS \cdot S \\ CO \end{smallmatrix} C : CH \cdot C_6H_4 \cdot NM_{e_2}$, orange-red plates, m. p. 219°, and 1-*p*-anisidyl-3-*p*-hydroxy-*m*-methoxybenzylidenes-rhodanine, $C_{15}H_{15}O_4NS_2$, pale orange-coloured, crystalline powder, m. p. 210°.

J. J. S.

Preparation of Formyl Derivatives of Morphine Alkaloids. FÄRGENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 222920).—The formyl derivatives of the morphine alkaloids are readily obtained by heating either the bases, their salts, or halogen compounds with formic acid or sodium formate, the alcoholic hydroxyl of the base being the point of attack.

Formylcodeine, colourless crystals, m. p. 180°, is prepared by boiling dry codeine with an excess of formic acid (100%) during five or six hours; it is insoluble in water, and sparingly so in alcohol and ether.

Formylmorphine is obtained by boiling together dry morphine hydrochloride (10 parts), sodium formate (5 parts), and formic acid (50 parts). It has m. p. 220° (about), and at 253° decomposes into its progenitors; the salts are crystalline. The formyl derivatives of morphine ether and of methylmorphinemethine can be similarly prepared.

F. M. G. M.

Preparation of Morphine Esters of Acylaromatic Hydroxy-carboxylic Acids. J. D. RIEDEL (D.R.-P. 224197).—When morphine is treated with the acid chlorides of acylphenolcarboxylic acids, compounds of the type $C_{17}H_{18}O_2N \cdot OCO \cdot R \cdot OR'$ (R = an arylene, R' = an acyl) and of great therapeutic value are produced.

p-Acetoxybenzoylmorphine, $C_{25}H_{25}O_6N$, long, prismatic needles sintering at 225°, m. p. 232° (with decomp.), was prepared as follows: *p*-Acetoxybenzoic acid, m. p. 196°, obtained from *p*-hydroxybenzoic acid and acetic anhydride, was treated with phosphorus pentachloride and the mixture distilled in a vacuum, yielding *p*-acetoxybenzoyl chloride, which after distillation at 161–162°/12 mm. solidified to long needles, m. p. 30°. This chloride (dissolved in chloroform) was slowly shaken with morphine in aqueous alkaline solution, the liquids separated, and the product obtained in crystalline form by the addition of ethylacetate. The methochloride, small prisms, was obtained by the action of methyl sulphate and sodium chloride on the base.

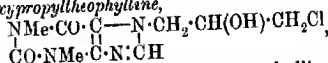
p-Methyl-carbonatobenzoylmorphine, $C_{26}H_{26}O_5N$, was analogously prepared from *p*-methyl-carbonatobenzoyl chloride (Fischer, Abstr., 1908, 94, i, 892); it forms colourless needles, m. p. 175–176° (with decomp.). The hydrochloride crystallises from either methyl or ethyl alcohol in large prisms containing one molecule of the respective alcohol of crystallisation, and with m. p. 165–190° (indefinite). When shaken with the requisite quantity of dilute alcoholic ammonia and kept at the ordinary temperature, the *p*-methyl-carbonato-group is eliminated, and *p*-hydroxybenzoylmorphine, $C_{24}H_{24}O_5N$, m. p. 230–237° (with

decomp.), separates out; the *hydrochloride* forms prismatic needles; the *methobromide*, small leaflets, was prepared by the action of methyl sulphate and potassium bromide in chloroform solution.

F. M. G. M.

Preparation of Halogenhydroxyalkyl-substituted Xanthine Bases. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.P. 224159).—When xanthine bases are treated with substituted halogen alkyl oxides, reaction occurs with the iminic hydrogen.

Chlorohydroxypropyltheophylline,

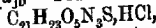


m. p. 141–143°, is prepared by heating theophylline with epichlorohydrin in a closed vessel at 130° during several hours with continual stirring; it is readily soluble in water, and when boiled with an alkaline hydroxide is converted into dihydroxypropyltheophylline.

F. M. G. M.

Strychnine Alkaloids. IX. Derivatives of Strychninesulphonic Acid I. and Oxidation of Bromostychnine. HERMANN LEUCHS and PAUL BOLL (*Ber.*, 1910, 43, 2362–2374. Compare Abstr., 1909, i, 120, 671).—The sulphonic acid group of strychninesulphonic acid is not attached to one of the benzene nuclei, and hence the acid readily yields substitution products, for example, mono- and di-chloro-derivatives, a monobromo-, a nitro- and a nitrobromo-derivative. Strychnine itself yields a hydrate of a dinitro-derivative, and it is probable that one of the nitro-groups of this derivative occupies the same position as the sulphonic group in strychninesulphonic acid. The nitrosulphonic acid is readily reduced to the corresponding amino-acid, and with alkaline reducing agents, azostychninesulphonic acid is also formed. So far it has not been found possible to prepare diazo- and hydroxy-compounds corresponding with the amino-derivative. The sulphonic acid group of strychninesulphonic acid is not removed by heating with concentrated hydrochloric acid, but an atom of chlorine is introduced: $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2\text{S} + \text{HCl} = \text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_2\text{S} + \text{H}_2\text{O}$, and this chloro-acid when boiled with water loses hydrogen chloride, yielding a product isomeric with the original sulphonic acid and termed isostrychninesulphonic acid I. The authors do not agree with the conclusion that the bromine atom in bromostychnine is attached to a carbon atom of a side-chain (Abstr., 1885, 911; Ciusa and Scagliarina, this vol., i, 583.)

Nitrostrychninesulphonic acid I, $\text{C}_{21}\text{H}_{22}\text{O}_7\text{N}_3\text{S}$, prepared by boiling the base for a short time with 5*N*-nitric acid in the presence of carbamide, crystallises in massive, straw-yellow prisms, which are not molten at 300°. It has $[\alpha]_D^{20} = -364^\circ$ in dilute sodium hydroxide solution. The corresponding amino-acid, $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}_3\text{S}$, crystallises in colourless needles or thin plates, and decomposes at 270°. Its solution in sodium hydroxide has $[\alpha]_D^{20} = -244.8^\circ$. The *hydrochloride*,



and sulphate are readily soluble, but the nitrate sparingly soluble.

Azostychninesulphonic acid I, $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_6\text{S}_2$, crystallises in orange-

yellow plates containing $8\text{H}_2\text{O}$, and when dehydrated under reduced pressure at 80° forms greenish-yellow crystals.

Bromostrychninesulphonic acid I., $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}_2\text{SBr}$, prepared by the action of a solution of bromine in hydrobromic acid (D 1.46) on the sulphonic acid, forms colourless, rectangular prisms or plates. In aqueous sodium hydroxide solution it has $[\alpha]_D^{20} - 233.6^\circ$.

Bromonitrostrychninesulphonic acid, $\text{C}_{21}\text{H}_{20}\text{O}_7\text{N}_3\text{SBr}\cdot\text{H}_2\text{O}$, formed by the action of bromine on the nitro-acid, crystallises in broad, yellow needles. Care is required in the preparation, as there is a tendency for the bromine to replace the nitro-group.

Chlorostrychninesulphonic acid I., $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}_2\text{SCl}\cdot\text{H}_2\text{O}$, is formed by the action of chlorine water and concentrated hydrochloric acid on the sulphonic acid at 0° , and crystallises in massive, six-sided prisms with $[\alpha]_D^{20} - 239.9^\circ$. *Dichlorostrychninesulphonic acid I.*,

$\text{C}_{21}\text{H}_{20}\text{O}_5\text{N}_2\text{SCl}_2\cdot\text{H}_2\text{O}$,
forms six-sided plates and has $[\alpha]_D^{20} - 155.9^\circ$.

Chloride of isostrychninesulphonic anhydride, $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_2\text{SCl}\cdot 2\text{H}_2\text{O}$, obtained by the action of concentrated hydrochloric acid on the sulphonic acid at $130\text{--}135^\circ$, crystallises in long prisms, loses its water of hydration at 80° under reduced pressure, and gives Otto's strychnine reaction. *isostrychninesulphonic acid I.*, $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}_2\text{S}\cdot 2\text{H}_2\text{O}$, has $[\alpha]_D^{20} - 242^\circ$ to -244° in alkaline solution, and is not so readily soluble in water as the isomeric acid. The *chloride of isonitrostrychninesulphonic anhydride I.*, $\text{C}_{21}\text{H}_{20}\text{O}_6\text{N}_3\text{SCl}$, crystallises in irregular plates, practically insoluble in water, and *isonitrostrychninesulphonic acid I.*, $\text{C}_{21}\text{H}_{21}\text{O}_7\text{N}_3\text{S}$, has $[\alpha]_D^{20} - 285.9^\circ$, and its solubility in water is 1 in 2000.

When oxidised with hydrogen peroxide, the sulphonic acid I. yields the *amino-oxide*, $\text{C}_{21}\text{H}_{22}\text{O}_6\text{N}_2\text{S}_2\cdot 2\text{H}_2\text{O}$, in the form of long, colourless needles, with $[\alpha]_D^{20} - 161.8^\circ$ in alkaline solution. It is readily reduced by sulphurous acid. The nitrosulphonic acid I. when oxidised in a similar manner yields the *amino-oxide*, $\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}_3\text{S}$, as massive, yellow needles, with $[\alpha]_D^{20} - 240^\circ$.

Bromostrychninonic acid, $\text{C}_{21}\text{H}_{19}\text{O}_6\text{N}_2\text{Br}$, prepared by oxidising bromostrychnine (Beckurts, Abstr., 1890, 1329) in acetone solution with permanganate, crystallises in twinned needles, is hydrated, has m. p. $274\text{--}276^\circ$ (corr.), and $[\alpha]_D^{20} - 54.8^\circ$ in alkaline solution. J. J. S.

Strychnine Alkaloids. X. Reactions of Strychninonic Acid and of Strychninolone. HERMANN LEUCHS and PAUL REICH (*Ber.*, 1910, 43, 2417—2429. Compare Abstr., 1908, i, 564; 1909, i, 602). —Attempts have been made to prove the presence of two carboxylic groups in strychninonic acid. With methyl alcohol and hydrogen chloride a monomethyl ester is formed, and ultimately products containing chlorine, and these with sodium carbonate yield two substances, one containing two carbomethoxy-groups and the other a carboxylic and a carbomethoxy-group, but both derived from the original acid plus a molecule of water, so that it is possible that the second carboxylic group is formed by the addition of water to an $\text{N}\cdot\text{CO}$ group in the original strychninonic acid molecule.

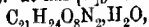
The acid reacts with dilute hydrochloric acid, yielding two hydrates containing respectively one and two molecules of water. The former

is regarded as an imino-acid formed by the rupture of the $\begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix}$ group. In the other, the second molecule of water is probably attached to the carbonyl group.

An anilide is formed when the acid is boiled with aniline, and hence the carbonyl group is in all probability not in the α -position with respect to the carboxylic group.

Methyl strychninonate, $\text{C}_{22}\text{H}_{22}\text{O}_6\text{N}_2$, crystallises from methyl alcohol in brilliant prisms, m. p. 247—249°. A *hydrate* of the methyl ester, $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_2$, is formed when the solution in methyl alcohol is saturated with hydrogen chloride, and crystallises in rectangular prisms or plates, m. p. 184—186°. It dissolves in both dilute acids and dilute alkalis. The *dimethyl ester hydrate* forms a platinichloride, probably $\text{C}_{46}\text{H}_{64}\text{O}_{14}\text{N}_4\text{PtCl}_6$.

Strychninonic acid hydrate, $\text{C}_{21}\text{H}_{22}\text{O}_7\text{N}_2$, crystallises from water in long needles containing $2\text{H}_2\text{O}$, which it loses at 105°, and then has m. p. 270—275° (decomp.). It has $[\alpha]_D^{20} + 39.6^\circ$. The *dihydrate*,



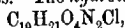
is less soluble in water, and crystallises at 0° in rectangular prisms; it has m. p. 235—240°. It yields a *sodium salt*, $\text{C}_{21}\text{H}_{22}\text{O}_7\text{N}_2\text{Na}$, which forms small prisms, m. p. 250—255° (decomp.).

Nitrostrychninonic acid, $\text{C}_{21}\text{H}_{19}\text{O}_8\text{N}_3$, obtained by the action of 5*N*-nitric acid and carbamide on strychninonic acid and extracting with chloroform, crystallises from glacial acetic acid in six-sided plates, m. p. 264—266° (decomp.). Yield, 20—25%.

Strychninonanilide, $\text{C}_{27}\text{H}_{26}\text{O}_5\text{N}_3$, crystallises from 75% acetic acid in short, massive prisms, m. p. 255° (decomp.).

Strychninolone contains a hydroxyl group, and yields an *acetyl derivative*, $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_2$, which crystallises from methyl alcohol in brilliant prisms, m. p. 126—128° (decomp.). With a chloroform solution of phosphoryl chloride, strychninolone yields *strychninolone chloride hydrate*, $\text{C}_{19}\text{H}_{19}\text{O}_5\text{N}_2\text{Cl}$, which crystallises from absolute alcohol in slender needles, m. p. 236°.

When heated with concentrated hydrochloric acid at 100°, strychninolone yields two hydrates. The *hydrochloride of hydrate I*,



crystallises from hot water in glistening prisms, m. p. 305—310° (decomp.). The hydrate itself is a syrup. The *hydrate II*,

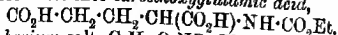


crystallises from water in thick prisms or long needles, m. p. 239—240°. Both hydrates have the properties of amino-acids.

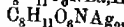
J. J. S.

Glutamic Acid and Pyrrolidonecarboxylic Acid. Engl. ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1910, 68, 487—503. Compare this vol., i, 230).—Owing to the ease with which it changes into glutamic acid, the formation of pyrrolidonecarboxylic (not pyrrolidinecarboxylic, *loc. cit.*) acid has not yet been detected amongst the products of the hydrolysis of albumins by the ordinary processes. With this end in view, the authors have instituted further experiments for the separation of pyrrolidonecarboxylic acid from

other amino-acids, especially from glutamic acid. Utilising the amino-group in the latter, the authors have converted it by means of ethyl chloroformate into *carbethoxyglutamic acid*,



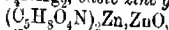
which forms a *barium salt*, $\text{C}_8\text{H}_{11}\text{O}_6\text{NBa}_2\cdot\text{H}_2\text{O}$, a *silver salt*,



and an amorphous, green *copper salt*, $\text{C}_8\text{H}_{11}\text{O}_6\text{NCu}$, which is much less soluble in water than copper pyrrolidonecarboxylate. It is noteworthy that glutamic acid, owing to the influence of the amino-group on the neighbouring carboxyl, behaves generally like a monobasic acid (*loc. cit.*), whereas carbethoxyglutamic acid exerts its dibasic function in salt formation. The separation of glutamic acid from pyrrolidonecarboxylic acid is very conveniently effected by Siegfried's carbanimino-reaction (Abstr., 1906, i, 144).

The formation of pyrrolidonecarboxylic acid from glutamic acid by heating has been examined more thoroughly. At $150-160^\circ$, *d*-glutamic acid yields a product, m. p. about 145° , $[\alpha]_D -10.06^\circ$ in water, from which *l*-pyrrolidonecarboxylic acid, $[\alpha]_D -11.5^\circ$, can be separated by fractional crystallisation from water. At $180-220^\circ$, *d*-glutamic acid yields chiefly *i*-pyrrolidonecarboxylic acid. At $160-170^\circ$, under conditions as yet unknown, *d*-glutamic acid yields occasionally a small quantity of a substance, $\text{C}_5\text{H}_7\text{O}_3\text{N}$, m. p. $180-182^\circ$, $[\alpha]_D +4.24^\circ$ in water. A *l*-pyrrolidonecarboxylic acid, obtained from *d*-glutamic acid and having $[\alpha]_D -11.27^\circ$ in water, had $[\alpha]_D +4.24^\circ$ in methyl alcohol and $+3.75^\circ$ in ethyl alcohol. A *l*-pyrrolidonecarboxylic acid, (therefore containing about 19% of the inactive acid), was treated with 5*N* hydrochloric acid for six to seven days, whereby *d*-glutamic acid, $[\alpha]_D +23.3^\circ$, was obtained; pure *d*-glutamic acid in 5*N*-hydrochloric acid has $[\alpha]_D +28.88^\circ$. Under similar conditions, *i*-pyrrolidonecarboxylic acid yielded *i*-glutamic acid hydrochloride, m. p. 200° .

Silver glutamate, $\text{C}_5\text{H}_7\text{O}_4\text{NAg}_2$, *basic zinc glutamate*,



and the *lead*, *copper*, and *silver salts* of pyrrolidonecarboxylic acid are described.

G. S.

Existence of Liquid Racemic Compounds. ALBERT LADENBURG and SOBECKI (*Ber.*, 1910, 43, 2374-2380).—The freezing-point curve of mixtures of *d*- and *l*-pipercolines has been determined; the curve shows two eutectics at -6.65° and a maximum at -4.9° , corresponding with the formation of a definite racemic compound.

The solubility of dipentene in 98.99% acetic acid at 12° has been determined, the method of estimation being conversion into bromide. The saturated solution of dipentene in acetic acid when shaken with 10% of d-limonene still shows the same amount of hydrocarbon in solution, although the solution has become strongly dextrorotatory. The two results are contradictory, but the authors conclude that dipentene is a mixture and not a definite compound.

Experiments have also been made on the solubility of *dl*-ethylpiperidine and mixture of *dl* with *l*-ethylpiperidine in water at 24.95° and 21.95° . The concentration of the solutions was determined by means of standard hydrochloric acid, using *o*-nitrophenol as

indicator. The results show that the solubility is not affected by the presence of an excess of one of the active constituents. The solution, however, was levorotatory.

Pure *l*- α -ethylpiperidine is best prepared by resolution of the *dl*-base with Reychler's acid. The *l*-base has D_{25}^D 0.8451, and $[\alpha]_D^{25}$ -21.3°.

Details of the preparation of the *dl*-base are given. J. J. S.

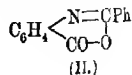
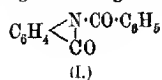
Anomalous Products of Benzoylation. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1910, 43, 2574—2581).—After quoting several instances in which anomalous products are obtained by benzoylation in pyridine or quinoline (Heller and Kiesselmann, *Abstr.*, 1902, i, 779; Heller, *Abstr.*, 1903, i, 827; Scholl and Berblinger, *Abstr.*, 1907, i, 257), the authors describe the following benzoylated substances containing pyridine. By treating a cold pyridine solution of *p*-aminobenzoic acid with benzoyl chloride, the substance, $2C_{14}H_{11}O_3N_3C_6NH_5$, m. p. above 340°, is obtained, which crystallises in slender needles, forms sparingly soluble sodium and potassium salts, and retains the pyridine even after steam has been passed through its strongly alkaline solution; the pyridine is removed, however, by hydrochloric acid at 170°, aniline and *p*-aminobenzoic acid being formed. Benzoylation in quinoline or dimethylaniline yields only the normal product. In a similar way, *m*-aminobenzoic acid and *p*-aminophenylacetic acid yield respectively the substances, $2C_{14}H_{11}O_3N_3C_6NH_5$ and



(which are precipitated by the addition of dilute hydrochloric acid), together with the normal products of benzoylation. When *p*-benzoylaminobenzoic acid is heated with acetic anhydride, an isomeride separates on cooling in tufts of colourless needles; it contains $\frac{1}{2}Ac_2O$, which is removed at 150°, but not by sodium carbonate solution, and has m. p. 240° (softening at 150—155° and resolidifying). The dried substance sinters at 265°, resolidifies, and then slowly decomposes at a much higher temperature; it is not immediately soluble in boiling sodium carbonate, and only dissolves slowly in warm sodium hydroxide, the solution yielding *p*-benzoylaminobenzoic acid by acidification. On account of these properties, the isomeride receives the constitution $C_6H_4 \begin{smallmatrix} \text{NH}_2Bz \\ \text{CO} \end{smallmatrix} O$, and is called *p*-benzoylaminobenzoic acid cycloid. When boiled with acetic anhydride, *p*-acetylaminobenzoic acid yields *p*-diacetylaminobenzoic anhydride, $(NAc_2 \cdot C_6H_4 \cdot CO)_2O$, m. p. 253—254°.

The paper also contains a reply to the statements of Bamberger (*Abstr.*, 1909, i, 509) and of Mohr (this vol., i, 116) that acetyl-anthranil contains the 1:3-oxazine ring. C. S.

Constitution of Benzoylanthranil. OTTO MUMM and RUGO HESSE (*Ber.*, 1910, 43, 2505—2511).—Two formulae have been proposed for benzoylanthranil: that of Friedländer and Wiegand (I), and that of Angeli and Angelico (II), of which the latter is considered the



more probable. No direct proof of its validity, however, has yet been given, but such is now afforded by the interaction of anthranilic acid with benzanilideiminochloride to form a ring system. From the intermediate product of the reaction, water must be eliminated if the Friedländer-Wiegand formula is correct, and aniline must be eliminated if the Angeli-Angelico formula is the true one. Experiments in absolute ethereal solution, with or without pyridine, proved that aniline is eliminated and benzoylanthranil formed.

Diphenylquinazoline, $C_6H_4 \begin{smallmatrix} \swarrow N \cdot CPh \\ \searrow CO \cdot NPh \end{smallmatrix}$, could not be obtained by the action of benzanilide chloride on anthranil, but it was obtained by shaking sodium anthranilate in aqueous solution with benzanilideiminochloride in ether. It crystallises in prisms, m. p. 158–159°, and has faintly basic properties, the *hydrochloride* having m. p. 172°. E. F. A.

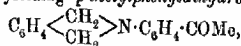
Preparation of Substituted Indoles by the Catalytic Decomposition of Arylhydrazones. ALEXANDER E. ARBUSOFF and W. M. TICHWINSKY (*Ber.*, 1910, 43, 2301–2303).—The phenyl- and tolylhydrazones of the lower aliphatic aldehydes and ketones yield substituted indoles when heated with small amounts (0.1 gram) of cuprous chloride at 180–230°. The bases can be isolated by subjecting the crude products to fractional distillation under reduced pressure.

2:3-Dimethylindole, 3-methylindole, and 3:5-dimethylindole have been prepared from methyl ethyl ketone phenylhydrazone, propionaldehyde-phenylhydrazone, and propionaldehyde-*p*-tolylhydrazone respectively.

Zinc chloride and platinous chloride can be used instead of cuprous chloride. J. J. S.

Syntheses with *o*-Xylylene Bromide. MAX SCHOLTZ and R. WOLFRUM (*Ber.*, 1910, 43, 2304–2318. Compare Scholtz, *Abstr.*, 1898, i, 305, 383, 471, 565, 567).—*tert*-Butylamine reacts with *o*-xylylene bromide in the same manner as other aliphatic primary amines, no steric hindrance is observable, and the product is *tert*-butyldihydroisindole, $C_6H_4 \begin{smallmatrix} \swarrow CH_2 \\ \searrow CH_2 \end{smallmatrix} N \cdot CMe_3$, which crystallises from ethyl alcohol in glistening plates, m. p. 42° and b. p. 125–130°/13 mm. Its *methiodide*, $C_{13}H_{20}NI$, forms colourless crystals, m. p. 221°.

p-Aminoacetophenone (3 mols.) also condenses with *o*-xylylene bromide (1 mol.), yielding *p*-acetylphenyldihydroisindole,



in the form of glistening plates, m. p. 197°. This compound condenses with aldehydes in the presence of alkalis in much the same manner as *p*-aminoacetophenone itself (Scholtz and Huber, *Abstr.*, 1904, i, 253).

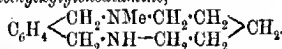
The *benzylidene* derivative, $C_6H_5 \cdot N \cdot C_6H_4 \cdot CO \cdot CH \cdot CHPh$, crystallises from alcohol in glistening, yellow plates, m. p. 202°; the *cinnamylidene* derivative, $C_6H_5 \cdot N \cdot C_6H_4 \cdot CO \cdot CH \cdot CH \cdot CH \cdot CHPh$, crystallises from

acetone in slender, orange-coloured needles, m. p. 187°; the *nitrobenzylidene* derivative, $C_{23}H_{18}O_3N_2$, forms a pale yellow, crystalline powder, m. p. 238°. 2-*p*-*Dimethylamino-p*-cinnamoylphenyldihydroisindole, $C_6H_5 \cdot N \cdot C_6H_4 \cdot CO \cdot CH : CH \cdot C_6H_4 \cdot NMe_2$, crystallises from pyridine in golden-yellow plates, m. p. 196°.

At 100° 2-phenyldihydroisindole combines readily with methyl iodide, yielding the *methiodide*, $C_8H_8 \cdot NPh \cdot MeI$, which forms colourless plates, m. p. 177°. 2-Phenyldihydroisindole condenses readily with aldehydes, especially in the presence of concentrated hydrochloric acid, yielding derivatives of diphenylmethane, or, in the case of aromatic aldehydes, derivatives of triphenylmethane. The condensation takes place in the para-position with respect to the nitrogen atom, as *p*-tolyldihydroisindole does not react with aldehydes. Formaldehyde reacts without the aid of a condensing reagent, yielding *biszylyleneaminodiphenylmethane*, $CH_2(C_6H_4 \cdot N : C_6H_5)_2$, which forms slender needles, m. p. 308–309°. *Biszylyleneaminotriphenylmethane*, $CHPh(C_6H_4 \cdot N : C_6H_5)_3$, separates from a mixture of pyridine and alcohol in colourless, felted needles, m. p. 265°. *Biszylyleneaminodimethylaminotriphenylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH(C_6H_4 \cdot N : C_6H_5)_2$, crystallises from pyridine in colourless needles, m. p. 185°. *Biszylyleneaminodiphenylstyrylmethane*, $CHPh \cdot CH : CH(C_6H_4 \cdot N : C_6H_5)_2$, forms a yellow, crystalline powder, which is not molten at 300°. *Biszylyleneamino-di-m-tolylmethane*, $CH_2(C_6H_3Me \cdot N : C_6H_5)_2$, obtained from *m*-tolyldihydroisindole, crystallises from pyridine in colourless needles, m. p. 255°.

Scholtz and Jaross (Abstr., 1901, i, 485) have shown that secondary 1:4-diamines condense with alcoholic solutions of aldehydes without the use of a condensing agent; an exception to this rule is xylylene-di-*o*-toluidine, which does not react. It is now shown that this base will condense with aldehydes in the presence of concentrated hydrochloric acid. With formaldehyde, it yields *methylene-di-o-tolyl-o-xylylenediamine*, $C_6H_4 \begin{smallmatrix} < CH_2 \cdot N(C_6H_4Me) \\ < CH_2 \cdot N(C_6H_4Me) \end{smallmatrix} > CH_2$, as glistening prisms, m. p. 139°, and with benzaldehyde, *benzylidene-di-o-tolyl-o-xylylenediamine*, $C_6H_4 \begin{smallmatrix} < CH_2 \cdot N(C_6H_4Me) \\ < CHPh \cdot N(C_6H_4Me) \end{smallmatrix} > CHPh$, m. p. 180°.

Methylamine reacts with xylylenepiperidonium bromide at 200° in much the same manner as ammonia (Abstr., 1898, i, 567), yielding *pentamethylenemethylxylylenediamine*,

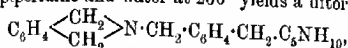


This is a colourless liquid, b. p. 160–165°/15 mm., and yields a *benzenesulphonyl* derivative, $C_{14}H_{21}N_5 \cdot SO_2Ph$, m. p. 87°. When distilled, the methyl derivative yields 2-methyldihydroisindole (Fränkel, Abstr., 1901, i, 45).

The products obtained by the condensation of xylylenepiperidonium bromide with aliphatic secondary amines, and previously represented as $NR_2 \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot N : C_6H_{10}$, are undoubtedly cyclic compounds of the type $C_6H_4 \begin{smallmatrix} < CH_2 \cdot NR \cdot CH_2 \cdot CH_2 \\ < CH_2 \cdot NR \cdot CH_2 \cdot CH_2 \end{smallmatrix} > CH_2$. Aromatic primary amines react with xylylenepiperidonium bromide in different ways

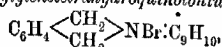
according to the nature of the amine. With aniline at 200°, piperidine and phenylidihydroisindole are formed; *p*-toluidine reacts in a similar manner, but *o*-toluidine does not yield an isindole derivative. The reaction probably consists of a rupture of the original ring, the formation of an eleven-membered ring, and the splitting up of this into the two compounds mentioned.

Dixylyleneammonium bromide (Scholtz, Abstr., 1891, 1353) when heated with piperidine and water at 200° yields a ditortary base,



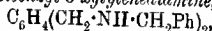
xylylenepentamethylenexylylenediamine, h. p. 240–245°.

o-Xylylene bromide and tetrahydroquinoline condense in the usual manner, yielding *o*-xylylenetetrahydroquinolinium bromide,



which is a syrup; the corresponding *iodide*, $\text{C}_{17}\text{H}_{18}\text{NI}$, forms colourless needles, m. p. 238°, and the *picrate*, $\text{C}_{17}\text{H}_{13}\text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$, yellow needles, m. p. 165°.

Dibenzyl-o-xylyleneammonium bromide, $\text{C}_8\text{H}_8 \cdot \text{NBr}(\text{CH}_2\text{Ph})_2$, prepared from *o*-xylylene bromide and dibenzylamine in chloroform solution, crystallises in snow-white plates, m. p. 188°, and when heated with ammonia at 200° yields *dibenzyl-o-xylylenediamine*,



the *hydrochloride* of which has m. p. 251°.

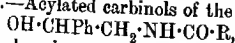
o-Xylylenediisocamylammonium bromide is an oil; the *iodide*, $\text{C}_{15}\text{H}_{20}\text{NI}$, crystallises from water, and has m. p. 139°. The bromide when heated with ammonia at 200° yields *o*-xylylenediisocamylamine, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NH} \cdot \text{C}_5\text{H}_{11})_2$, a colourless oil with b. p. 210°/12 mm.

Dibenzylpiperidonium bromide, $\text{C}_8\text{H}_{10} \cdot \text{NBr}(\text{CH}_2\text{Ph})_2$, prepared by the action of dibenzylamine on *ac*-dibromopentane, crystallises in colourless plates, m. p. 253°, and when heated with ammonia at 200° yields benzylamine, dibenzylamine, and benzylpiperidine. *o*-Xylylenedipropylammonium bromide, $\text{C}_8\text{H}_8 \cdot \text{NBr}(\text{C}_3\text{H}_7)_2$, crystallises in colourless plates, m. p. 107°, and when heated with ammonia at 200° yields propyl bromide and 2-propyldihydroisindole. The latter is a colourless oil, b. p. 230–240°, and forms a *methiodide*, $\text{C}_{11}\text{H}_{15}\text{N} \cdot \text{MeI}$, m. p. 150°. The *platinichloride*, $(\text{C}_{11}\text{H}_{15}\text{N})_2\text{H}_2\text{PtCl}_6$, forms a reddish-yellow powder, m. p. 192°. The decomposition of the dipropyl derivative is thus analogous to that of the diethyl salt (Abstr., 1898, i, 568).

2 *Amylenedihydroisindole*, $\text{C}_8\text{NH}_8 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, obtained by treating xylylenepiperidonium bromide with moist silver oxide evaporating to a syrup, and distilling, has h. p. 140–150°/12 mm. Its *methiodide* is also oily.

J. J. S.

New Method for the Synthesis of *iso*Quinoline Bases. AMÉ PICTET and ALFONS GAMS (*Ber.*, 1910, 43, 2384–2391. Compare Abstr., 1909, i, 671).—Acylated carbinols of the type



where R = methyl, phenyl or benzyl, readily undergo condensation when heated with phosphoric oxide and xylene, yielding 1-substituted

isoquinolines. Phenylformylaminomethylcarbinol reacts in a similar manner, yielding *isoquinoline*, and this is the most convenient synthetic method for the preparation of the base.

Phenylphenacetylaminomethylcarbinol,
 $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Ph}$,

obtained by reducing ω -phenylacetylaminoacetophenone (Robinson, Trans., 1909, 95, 2167) with sodium amalgam, alcohol, and acetic acid, crystallises from water in slender needles, m. p. 123° .

Phenylbenzoylaminoethylcarbinol (Kolshorn, Abstr., 1904, i, 675) is prepared most readily by reducing benzoylaminoacetophenone (Robinson, loc. cit.). *Phenylacetylaminomethylcarbinol*,
 $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NHAc}$,

crystallises from benzene in colourless needles, m. p. 104° . 1-Benzyl-*isoquinoline* forms colourless needles, m. p. 56° . 1-*Phenylisoquinoline*, $\text{C}_{15}\text{H}_{11}\text{N}$, crystallises from dilute alcohol in colourless needles, m. p. 93° , b. p. $298^\circ/729$ mm. The *hydrochloride* has m. p. $235\text{--}236^\circ$; the *picrate*, m. p. $164\text{--}5^\circ$, and the *platinichloride* forms red needles, m. p. 242° (decomp.).

1-*Methylisoquinoline*, $\text{C}_{10}\text{H}_9\text{N}$, is a colourless oil, b. p. $243\text{--}245^\circ/728$ mm. The *hydrochloride* forms colourless needles, m. p. about 170° ; the *sulphate* forms colourless prisms, m. p. 245° ; the *picrate* has m. p. $206\text{--}208^\circ$; the *dichromate* forms red prisms, sparingly soluble in water, and decomposes at about 150° ; the *platinichloride*,
 $2\text{C}_{10}\text{H}_9\text{N}\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$,

forms reddish-yellow prisms, and melts at $201\text{--}5^\circ$ when anhydrous. The base is probably identical with the two methyl-*isoquinolines* described in Beilstein.

ω -*Formylaminoacetophenone*, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$, prepared by the action of crystallised formic acid on ω -aminoacetophenone hydrochloride, crystallises from a mixture of benzene and light petroleum in large, flat prisms, m. p. $70\text{--}71^\circ$, and when reduced with sodium amalgam, alcohol, and formic acid yields *phenylformylaminomethylcarbinol*, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$, as a reddish-brown, crystalline mass. J. J. S.

Preparation of a Dihydroxycarbazoledisulphonic Acid. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.P. 224953).—The product obtained by fusing carbazoledisulphonic acid with an alkali hydroxide has been described (Schultz and Hauenstein, Abstr., 1907, i, 1074), but whether the product was a dihydroxy- or a hydroxycarbazolesulphonic acid is not definitely stated.

When carbazole is treated with fuming sulphuric acid (five parts) at a temperature not exceeding 40° , and then slowly heated to 100° , *disulphonation* takes place; if this mixture is further treated with two parts of sulphuric acid (containing 65% SO_3) and kept at $90\text{--}100^\circ$ until the product ceases to be separable on the addition of salt, *carbazoletetrasulphonic acid* is obtained, and finally isolated by evaporation in the form of its *potassium salt*.

Dihydroxycarbazoledisulphonic acid is prepared from the foregoing acid by fusion with alkali hydroxide at a temperature of $240\text{--}300^\circ$.

the potassium salt forms colourless needles containing $4\text{H}_2\text{O}$, and shows a green fluorescence on addition of ammonium hydroxide.

The free acid can be isolated from its barium salt.

F. M. G. M.

[Preparation of *N*-Alkyl- and of *N*-Aryl-carbazoles and their Indophenol Derivatives.] LEOPOLD CASSELLA & Co. (D.R.P. 224951).—The *N*-alkyl-carbazoles have been previously described; it is now found that *N*-aryl-carbazoles can be prepared in analogous manner, and that they likewise, when heated with polysulphides, yield valuable dyes.

3-Benzylcarbazole, colourless needles, m. p. 118—120°, is prepared by the action of benzyl chloride on potassium carbazole at high temperatures or under pressure.

3-Phenylcarbazole is obtained by heating potassium carbazole with bromobenzene in the presence of copper powder under pressure at a temperature of 180—220°; it forms colourless needles, m. p. 82—84°.

9-*p*-Tolylsulphonylcarbazole, pale yellow needles, m. p. 127—128°, is prepared from potassium carbazole and *p*-toluenesulphonyl chloride. These substances combine with *p*-nitrosophenol, yielding dark blue powders, which on reduction form greyish-white, crystalline leuco-compounds.

F. M. G. M.

Condensation Products from Salicylidene- and Hydrocyano-salicylidene-aniline (Anilino-*o*-hydroxyphenylacetoneitrile). (GEORG RÖHDE and G. SCHARTEL (*Ber.*, 1910, 43, 2274—2286).—Miller and Plüchl (*Ber.*, 1896, 27, 1730; 1898, 29, 2699) have shown that Schiff's bases do not undergo the benzoin condensation with potassium cyanide. The product obtained by Schwab (*Abstr.*, 1901, i, 380) by condensing *o*-hydroxybenzylideneaniline with an alcoholic solution of potassium cyanide is shown to be 4-cyano-3-phenyl-2-*o*-hydroxyphenyl-3:4-dihydro-1:3-benzoxazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{CH}(\text{CN}) \cdot \text{NPh} \end{smallmatrix}$, and not

to have the constitution ascribed to it by Schwab. The product is prepared most readily by shaking vigorously for three hours an alcoholic solution of aniline (1 mol.) and salicylaldehyde (2 mols.) with an alcoholic solution of potassium cyanide (1 mol.). When its ethereal solution is hydrolysed with concentrated hydrochloric acid, the products are salicylaldehyde and the acid amide hydrocyanosalicylideneaniline, anilino-*o*-hydroxyphenylacetamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NHPh}) \cdot \text{CO} \cdot \text{NH}_2$, which yields a hydrochloride, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{HCl}$, crystallising from alcohol in colourless needles, m. p. 183°. The amide crystallises from benzene in colourless needles containing benzene and melting at 63°; when further heated, it gives up benzene, solidifies, and then has m. p. 126°. The same amide can be prepared by adding Miller and Plüchl's hydrocyanosalicylideneaniline (anilino-*o*-hydroxyphenylacetoneitrile) to concentrated hydrochloric acid.

Schwab's condensation product can be synthesised by shaking an alcoholic solution of hydrocyanosalicylideneaniline with salicylaldehyde and potassium hydroxide dissolved in a little water. The following derivatives are described: Sodium salt, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_2\text{Na}$, yellow,

glistening powder, m. p. 249°, obtained by shaking an ethereal solution of the 1:3-benzoxazine with 10% sodium hydroxide solution; *benzoyl* derivative, $C_{26}H_{20}O_8N_2$, yellow crystals, m. p. 188°; *benzenesulphonyl* derivative, $C_{27}H_{20}O_9N_2S$, glistening needles from alcohol, m. p. 162°.

Hydrocyanosalicylideneaniline and benzaldehyde undergo condensation in the presence of potassium hydroxide, yielding 4-cyano-2:3-diphenyl-2:4-dihydro-1:3-benzoxazine, $C_{14}H_{13}ON_2$, in the form of yellow needles, m. p. 138°.

When molecular quantities of salicylideneaniline and potassium cyanide are condensed, a product, $C_{14}H_{13}ON_2$, is formed, which crystallises from benzene in compact prisms, m. p. 135–137°. The same product is formed by condensing salicylaldehyde and salicylideneaniline with potassium cyanide or salicylideneaniline and hydrocyanosalicylideneaniline with potassium cyanide. It is isomeric with hydrocyanosalicylideneaniline, from which it can be obtained by shaking with potassium cyanide, potassium carbonate, or sodium ethoxide solutions.

A by-product formed in the preparation of the benzoxazine separates as dark red needles from the mother liquors after a time, and can be obtained most readily by boiling an alcoholic solution of aniline, salicylaldehyde, and potassium cyanide for two to three hours. It can be crystallised from pyridine, has m. p. 258°, and is stable towards acids. Its *acetyl* derivative crystallises from alcohol in pale yellow needles, m. p. 195°, and its *benzoyl* derivative in yellowish-brown prisms, m. p. 227°.

J. J. S.

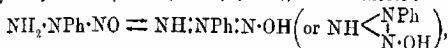
Catalytic Decomposition of Phenylhydrazine by means of Cuprous Halides. ALEXANDER E. ARBUSOFF and W. M. TICHWINSKY (*Ber.*, 1910, 43, 2295–2296. Compare Struthers, *Proc.*, 1905, 21, 95).—At 150° phenylhydrazine reacts with cuprous halides according to the equation: $3NHPh \cdot NH_2 + CuCl = 3NH_2Ph + N_2 + NH_3 + CuCl$. The reaction is preceded by the formation of an additive compound, for example, the compound, $2NHPh \cdot NiCl_2 \cdot CuI$, has been isolated as colourless prisms, which begin to decompose at 150°.

The rate of decomposition with the different halides has been determined; the reaction proceeds most rapidly with the chloride, and least readily with the iodide. If sufficient care is not taken, the reaction with cuprous chloride may become explosive. J. J. S.

Nitrosophenylhydrazine. EUGEN BAMBERGER and H. HAUSER (*Annalen*, 1910, 375, 316–333).—The preparation and properties of nitrosophenylhydrazine are described, and also many of its reactions, chiefly in the form of test-tube experiments. It acts as a pronounced reducing agent towards mercuric nitrate, yellow mercuric oxide, silver nitrate, and calcium hypochlorite, being itself oxidised mainly to nitrobenzene (detected by its odour). Its alcoholic solution, as concentrated as possible, yields at -12° to -15° with a cold saturated alcoholic solution of cupric acetate, *copper nitrosophenylhydrazine*, $Cu(C_6H_5N_2O)_2$, which forms copper-red leaflets with a bronze lustre, is extremely explosive, and inflames in contact with concentrated sulphuric or nitric acid. The solution of the metallic derivative in

acetone gives, almost immediately, a precipitate of copper sulphide with hydrogen sulphide; the reaction, however, is not regarded as ionic, the substance being probably an internally complex salt. When the red copper derivative is treated with acetic acid containing a little water (the absence of water prevents the reaction), nitrogen is evolved and pale grey needles of copper nitrosophenylhydroxylamine are produced. This copper derivative is more conveniently obtained by treating an alcoholic solution of nitrosophenylhydrazine at 0° with a solution (saturated at 5°) of copper acetate in glacial acetic acid (the reaction fails in the presence of 13–15% of water), or by adding nitrosophenylhydrazine to ammoniacal copper hydroxide at -16°. This indirect conversion of nitrosophenylhydrazine into nitrosophenylhydroxylamine is not a case of simple hydrolysis: $\text{NH}_2\cdot\text{NPh}\cdot\text{NO} + \text{H}_2\text{O} = \text{OH}\cdot\text{NPh}\cdot\text{NO} + \text{NH}_3$, since it is not appreciably brought about by alkaline reagents, but is probably due to oxidation by the copper oxide: $\text{NH}_2\cdot\text{NPh}\cdot\text{NO} + \text{O} \rightarrow \text{OH}\cdot\text{NPh}\cdot\text{NO} + \text{N}_2$.

The paper closes with some adverse criticisms of the symmetrical formula, $\text{NPh}\cdot\text{NH}\cdot\text{NO}$, suggested by Thiele for nitrosophenylhydrazine in consequence of its decomposition into aniline and nitrous oxide; in the authors' opinion nitrosophenylhydrazine, like nitrosophenylhydroxylamine (Abstr., 1909, i, 977), is tautomeric:



its compounds with heavy metals being derived from either of the latter formulae. C. S.

Constitution of Nitrosophenylhydrazine. JOHANNES THIELE and KARL SIEGLITZ (*Annalen*, 1910, 375, 334–335).—The suggestion advanced by Thiele (Abstr., 1908, i, 927), that nitrosophenylhydrazine has the constitution $\text{NPh}\cdot\text{NH}\cdot\text{NO}$ has been withdrawn, because benzoylnitrosophenylhydrazine, obtained by the benzoylation of nitrosophenylhydrazine, is converted by stannous chloride and hydrochloric acid into *s*-benzoylphenylhydrazine, from which the benzoylnitrosophenylhydrazine is regenerated by sodium nitrite and acetic acid.

C. S.

α -Acylated Phenylhydrazines. OSKAR WIDMANN (*Ber.*, 1910, 43, 2595).—The author's method of preparing α -acylated phenylhydrazines (Abstr., 1893, i, 411; 1894, i, 57, 512; 1895, i, 31) has been overlooked by Lockemann (this vol., i, 636).

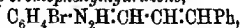
C. S.

Influence of the Halogens on Phototropy in Hydrazones. F. GRAZIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 190–193. Compare this vol., i, 509).—Some hydrazones derived from *p*-bromophenylhydrazine have been prepared to ascertain if the lack of phototropy in certain chloroaniline derivatives (compare Senior and Shepherd, *Trans.*, 1909, 95, 1943) is due to the presence of the halogen. Of the eight hydrazones examined, four are more or less phototropic, but much less so than the *p*-tolylhydrazones.

Benzaldehyde-*p*-bromophenylhydrazone has m. p. 129° (Biltz and Sieden, Abstr., 1903, i, 120, gave 127.5°), and is phototropic.

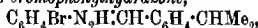
Anisaldehyde-*p*-bromophenylhydrazone, m. p. 150° (Ott, Abstr., 1905, i, 376, gave 146—147°), is not phototropic.

Cinnamaldehyde-*p*-bromophenylhydrazone,



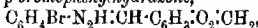
crystallises in greenish-yellow, lustrous needles, m. p. 143°, and is phototropic.

Cuminaldehyde-*p*-bromophenylhydrazone,



forms yellow, phototropic needles, m. p. 135°.

Piperonaldehyde-*p*-bromophenylhydrazone,



crystallises in colourless laminae, m. p. 155° (decomp.), and is not phototropic.

p-Tolualdehyde-*p*-bromophenylhydrazone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$,

forms small, yellow laminae, m. p. 162° (decomp.), and is not phototropic.

Vanillin-*p*-bromophenylhydrazone is non-phototropic.

Salicylaldehyde-*p*-bromophenylhydrazone has m. p. 171—172° (Biltz and Sieden, *loc. cit.*, gave 175·5°), and is slightly phototropic.

R. V. S.

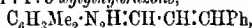
Relations between Constitution and Phototropy. MAURICE PANO and F. GRAZIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 193—196. Compare this vol., i, 509, and preceding abstract).—The authors have obtained a number of hydrazones derived from 1:4:5- and 1:3:5-xylylhydrazines, and have prepared the latter substances for the first time. In agreement with the regularity previously observed, the 1:4:5-derivatives do not exhibit phototropy. Of the four 1:3:5-compounds, one is very feebly phototropic.

1:4:5-Xylylhydrazine hydrochloride has m. p. 209°; Plancher and Caravaggi (Abstr., 1905, i, 158) gave 206°.

Benzaldehyde-1:4:5-xylylhydrazone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\text{H}\cdot\text{CHPh}$, forms small, yellow needles, m. p. 89°.

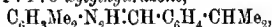
Anisaldehyde-1:4:5-xylylhydrazone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, crystallises in small, yellowish-white laminae, m. p. 117°.

Cinnamaldehyde-1:4:5-xylylhydrazone,



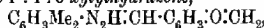
forms small, yellow needles, m. p. 121°.

Cuminaldehyde-1:4:5-xylylhydrazone,



crystallises similarly, and has m. p. 85°.

Piperonaldehyde-1:4:5-xylylhydrazone,



crystallises in yellow scales, m. p. 135°.

p-Tolualdehyde-1:4:5-xylylhydrazone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$,

forms minute, pale yellow scales, m. p. 109°.

Vanillin-1:4:5-xylylhydrazone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$,

crystallises in very small, colourless needles, m. p. 158°.

Salicylaldehyde-1:4:5-xylylhydrazone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, forms pale yellow scales, m. p. 134°.

1:3:5-Xylylhydrazine hydrochloride was prepared by diazotisation

of the corresponding xylidine. It is very soluble in concentrated hydrochloric acid, and was not obtained in pure condition.

Cinnamaldehyde-1:3:5-xylidylhydrazone forms yellow crystals, m. p. 142—143° (becoming slightly brown), and is phototropic.

p-Tolualdehyde-1:3:5-xylidylhydrazone crystallises in rosettes of yellow needles, m. p. 119°, and is not phototropic.

Piperonaldehyde-1:3:5-xylidylhydrazone forms yellow, non-phototropic needles, m. p. 135—136° (yielding a brown liquid).

Anisaldehyde-1:3:5-xylidylhydrazone crystallises in small, yellow needles, m. p. 144—145° (giving a brown liquid). R. V. S.

Preparation and Phototropy of Some Osazones. MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 302—307. Compare Padoa and Graziani, this vol., i, 509).—Continuing the study of phototropy, the authors have prepared osazones from benzil and piperil with *o*- and *p*-tolyl- and β -naphthyl-hydrazines. Even on combining these results with those of Biltz (Abstr., 1900, ii, 125), no connexion between constitution and phototropy becomes evident. Of the two isomeric forms to be expected, only the β -modification was obtained in every case.

β -Benzil-*p*-tolylsazone, $C_6H_5(C_6H_3(N \cdot NH \cdot C_6H_4Me)_2)_2$, obtained by Pickol's method (Abstr., 1886, 545), is a yellow, crystalline, phototropic substance, m. p. 152°.

β -Piperil-*p*-tolylsazone, $CH_3 \cdot O_2 \cdot C_6H_3 \cdot C \cdot N \cdot NH \cdot C_6H_4Me$
 $CH_3 \cdot O_2 \cdot C_6H_3 \cdot C \cdot N \cdot NH \cdot C_6H_4Me$ similarly prepared, crystallises in small, sulphur-yellow needles, m. p. 215°, and is phototropic.

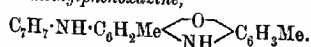
β -Benzil- β -naphthylsazone, $C_6H_5(C_{10}H_7(N \cdot NH \cdot C_{10}H_7)_2)_2$, obtained by the same method, forms yellow needles, m. p. 211.5°. It is phototropic, and one specimen of it showed phototropic change in either direction with remarkable rapidity, possibly owing to the presence of some impurity catalytically affecting the process.

β -Piperil- β -naphthylsazone, similarly prepared, is a yellow, crystalline, phototropic substance, m. p. 207°.

β -Benzil-*o*-tolylsazone was prepared by Purgotti's method (*Gazzetta*, 1892, 14, ii, 611), and forms a canary-yellow, crystalline, phototropic powder, m. p. 170°.

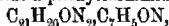
β -Piperil-*o*-tolylsazone, obtained by the same method, is a yellow, crystalline powder, m. p. 206.5°, and is phototropic. It becomes bright red instantly in sunlight, and may be said to be the most sensitive phototropic substance yet prepared. R. V. S.

Rearrangement in the Quinone Group. ERNST BÖRNSTEIN (*Ber.*, 1910, 43, 2380—2384).—The base obtained by the action of sulphuric acid on *p*-toluidino-*p*-toluquinonetolylimide (Abstr., 1901, i, 376) has the same composition as the original compound, and is regarded as 7-*p*-toluidino-3:6-dimethylphenoxazine,



It crystallises from ethyl alcohol or dilute acetone in brownish, orange-yellow needles or plates, m. p. 173°. The hydrochloride, $C_{21}H_{20}N_2 \cdot HCl$,

forms red rhombohedra, with a greenish, metallic reflex. The *platinichloride*, $2\text{C}_{21}\text{H}_{20}\text{ON}_2\cdot\text{H}_2\text{PtCl}_6$, has a yellowish-red colour. The *sulphate*, $\text{C}_{21}\text{H}_{20}\text{ON}_2\cdot\text{H}_2\text{SO}_4$, crystallises from alcohol in deep, red compact cubes. The *picrate*, $\text{C}_{27}\text{H}_{25}\text{O}_8\text{N}_5$, forms golden-yellow, microscopic needles, m. p. 227° . The base yields a phenylcarbimide derivative,



as colourless rosettes of needles, m. p. 188° (decomp.).

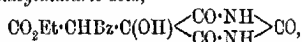
Attempts to acetylate, methylate, and form an oxims gave negative results. When reduced, the base yields *p*-toluidine. J. J. S.

Preparation of 5:5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.P. 225457).—The action of oxalyl chloride on dialkylmalonamides affords 78–80% of the theoretical yield of the respective dialkylbarbituric acid.

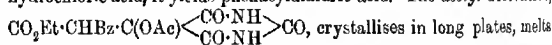
Equal weights are heated together on the water-bath during several hours, water is added, and the product collected. F. M. G. M.

Condensation Products of Alloxan. OTTO KÜHLING (*Ber.*, 1910, 43, 2406–2417. Compare *Abstr.*, 1905, i, 944; 1908, i, 571; Kühling and Schneider, *ibid.*, 1909, i, 424).—Alloxan condenses with ethyl benzoylacetate or the corresponding methyl ester in the presence of a mixture of water and alcohol, saturated at -6° to -8° , with hydrogen chloride, yielding carbethoxy- or carbomethoxy-phenacyldialuric acid. These compounds resemble the phenacyldialuric acids as regards their behaviour towards dilute acids or acetic anhydride, but are readily decomposed into their components when boiled with water, mixed with sodium carbonate solution at the ordinary temperature, or treated with the usual reagents for ketones. The acetyl derivatives, are more stable, and react with sodium carbonate solution, yielding compounds which are regarded as carbethoxy(methoxy)-phenacylbarbituric acids.

Carbethoxyphenacyldialuric acid,



crystallises from alcohol in rhombic prisms, m. p. $207\text{--}208^\circ$ (decomp.) after turning red at 180° . When boiled for several hours with 12% hydrochloric acid, it yields phenacyldialuric acid. The *acetyl* derivative,



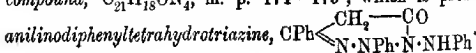
crystallises in long plates, melts at $167\text{--}168^\circ$, then solidifies, and melts again at $235\text{--}236^\circ$. *Carbethoxy*

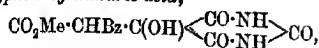
phenacylbarbituric acid, $\text{CO}_2\text{Et}\cdot\text{CHBz}\cdot\text{CH}\begin{matrix} \diagup \text{CO}\cdot\text{NH} \\ \diagdown \text{CO}\cdot\text{NH} \end{matrix} \text{CO}$, crystallises

from alcohol in prisms, m. p. $239\text{--}240^\circ$, and is also formed when the acetyl derivative is heated at $180\text{--}190^\circ$. It yields a *sodium salt*,

$\text{C}_{15}\text{H}_{13}\text{O}_6\text{N}_2\cdot\text{Na}$, in the form of prismatic needles, and reacts with benzenediazonium chloride solution, yielding alloxanphenylhydrazones.

With phenylhydrazine in acetic acid solution, the barbituric acid yields a yellow, amorphous precipitate, and yellowish-red crystals of a compound, $\text{C}_{21}\text{H}_{18}\text{ON}_4$, m. p. $174\text{--}175^\circ$, which is probably a *keto-*



Carbomethoxyphenacyldialuric acid,

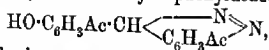
forms colourless prisms, m. p. 221° (decomp.). The acetyl derivative, $\text{C}_{14}\text{H}_{14}\text{O}_8\text{N}_2$, also forms prisms, melts at 158° , resolidifies, and again melts at $241\text{--}242^\circ$. *Carbomethoxyphenacylbarbituric acid*, $\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_2$, forms colourless needles, m. p. $246\text{--}247^\circ$ (decomp.). J. J. S.

Compounds of Piperazine with Phenols. H. STÉVIGNON (*Bull. Soc. chim.*, 1910, [iv], 7, 922—926).—Schmidt and Wichmann have shown that piperazine forms additive compounds with phenol and with quinol (Abstr., 1892, 210), and the author has extended this observation to other phenols, and finds that 1 mol. of piperazine combines with 2 mols. of a monohydric phenol or with 1 mol. of a dihydric phenol. In all cases the two substances were allowed to react in alcohol.

The following substances were prepared: *Di-o-cresolpiperazine*, m. p. $51\text{--}52^\circ$ (approx.), pale yellow crystals. *Dicarvacrolpiperazine*, m. p. $85\text{--}86^\circ$ (approx.), colourless needles. *Dithymolpiperazine*, m. p. 88° , brilliant, colourless needles. *Di-β-naphtholpiperazine*, m. p. 110° (approx.), greyish-white crystals. *Catecholpiperazine*, bright brown needles. *Diquaiacolpiperazine*, m. p. 98° (approx.), brilliant colourless lamellae. The piperazine in these compounds behaves as a diacidic base, and can be titrated directly with *N*/10-sulphuric acid, using helianthin-4 as indicator. T. A. H.

Action of Sulphuric and Hydrochloric Acids on *endo*Bisazo-derivatives. I. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 915—922).—It is shown that under the action of sulphuric or hydrochloric acid, the *endo*bisazo-compounds behave like azodiazocompounds, one azo-group being replaced by a hydroxyl group, which in the case of hydrochloric acid is then replaced by chlorine, whilst the second remains intact. Instances of this reaction have been given already (Abstr., 1907, i, 663), and are now repeated with experimental details. The author suggests that the substances now called indazoles should be re-named *isonzindoles*, and that the present *iso*azindoles should be named *azindoles*.

When 4:4'-diacetylbisazodiphenylmethane [4:6'-diacetylphenylbenzisindazole] (Abstr., 1908, i, 706) is heated with a 53% solution of sulphuric acid at $100\text{--}105^\circ$, it is converted in the course of a few minutes into 2'-hydroxy-4:6'-diacetyl-3-phenylbenzisindazole,



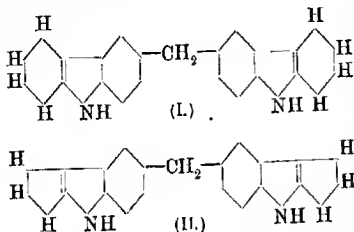
which in the author's new nomenclature would be "2'-hydroxy-4:6'-diacetyl-3-phenylindazole." It melts at 235° , forms bright yellow needles from alcohol, and is soluble in dilute sodium hydroxide solution, but not in ammonia. T. A. H.

Quinoline and Indole Derivatives from *para*Diaminodiphenylmethane. WALTHER BORSCHKE and G. A. KIENITZ (*Ber.*, 1910, 43, 2333—2337).—6:6'-*Diquinolylmethane*, $\text{CH}_2(\text{C}_9\text{NH}_8)_2$, can be prepared from *p*-diaminodiphenylmethane by the usual Skraup synthesis. It

forms a limpid, brown oil, which solidifies slowly, and can be obtained as colourless needles, m. p. 160°.

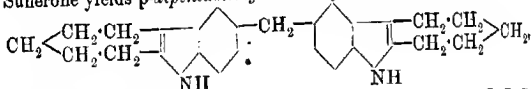
4:4'-*Dihydrazinodiphenylmethane*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2)_2$, prepared by diazotising β -diaminodiphenylmethane and reducing the diazo-compound by Fischer's method, crystallises from benzene in colourless plates, m. p. 71—72°, but turns brown in the course of a few hours when exposed to the air. The *hydrochloride* forms a white, crystalline powder, and is somewhat more stable. The *dibenzylidene* derivative, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CHPh})_2$, crystallises from glacial acetic acid in golden-yellow plates, m. p. 193—194°. The condensation product with dextrose, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CH}[\text{CH}\cdot\text{OH}]_4\cdot\text{CH}_2\cdot\text{OH})_2$, is a dark yellow, crystalline powder, m. p. 122—123° (decomp.).

The condensation product with *cyclohexanone* readily loses ammonia when warmed with glacial acetic acid (Abstr., 1908, i, 365), and yields *p-di- $\alpha\beta$ -tetramethyleneindolylmethane* (*bis*tetrahydrocarbazolylmethane, formula I.), which separates from dilute acetone in yellow crystals, m. p. 265°. From



cyclopentanone, *p-di- $\alpha\beta$ -trimethyleneindolylmethane* (formula II) is formed in a similar manner; it separates from dilute acetic acid in a yellow powder, m. p. 262°.

Suherone yields *p-dipentamethyleneindolylmethane*,

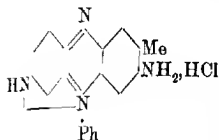


which does not melt at 300°.

J. J. S.

Synthesis of the Safranines. W. G. SAFOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 505—512. Compare Barbier and Sisley, Abstr., 1905, i, 840).—The author disagrees with the ordinarily accepted view of the formation of the safranines and indulines, namely, that the first products of the reaction are indamines which then condense with the amines. *p*-Benzoquinonedi-imide is quite inert towards amines, only reacting when one of the hydrogen atoms of the amino-group is displaced by a halogen, and this the more readily the greater the atomic weight of the halogen. It is, therefore, probable that the first product in the formation of the safranines is *p*-benzoquinonedi-chlorodi-imide (or a similar compound), which then reacts with the amines. The tertiary amines only form these condensation products when they have the property of readily losing one of their radicals. The secondary and primary amines are equally active, although some primary amines, such as tribromoaniline and dibromotoluidine, do not react at all or with difficulty. In all cases an excess of the amine is favourable to a good yield, and as the molecular weight of the amine increases, the number of molecules

of the amine that combine with one of the *p*-benzoquinonedichlorodi-imide decreases. Polyamines, particularly *m*-diamines, react readily with *p*-benzoquinonedichlorodi-imide. If in a mixed secondary and primary amine, a methyl group is introduced in an ortho-position to the primary amino-group, the compound so formed reacts very readily with *p*-benzoquinonedichlorodi-imide. Thus 4-phenyltolylene-2:4-diamine reacts readily with the quinone, forming the leuco-compound of indamine, which passes readily into indamine and then by loss of the



obtaining safranines is claimed to be far better than any method hitherto described.

heavier amino-group can be converted into the azone (annexed formula), which is the formula proposed for safranine. Its advantages over the formula hitherto accepted are discussed. Thus it readily explains why only one amino-group reacts when safranine is diazotised; also, why only a monoacetyl derivative is obtained and so forth. This method of Z. K.

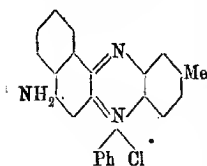
Synthesis of the Simplest Safranin: 3:6 Diamino 5-phenazonium Chloride. W. G. SAPOSHNIKOFF and N. N. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 512—522. Compare preceding abstract).—3:6-Diamino-5-phenyl-2-methylphenazonium chloride was prepared by heating a mixture of *p*-benzoquinonedichlorodi-imide (1 mol.) and 4-phenyltolylene-2:4-diamine (2 mols.) in alcoholic solution on a water-bath for fifteen to twenty minutes. The yield is 86.7—93.2% of the theoretical. The substance forms bright yellow crystals soluble in concentrated sulphuric acid with an emerald-green colour, turning violet and red on dilution. The base is precipitated by alkali hydroxides, but not by alkali carbonates, and is readily soluble in water. The *nitrate* and *chromate*, $(C_{19}H_{17}N_4)_2Cr_2O_7$, were prepared.

The *dinecyl* derivative, $C_{24}H_{21}O_2N_4Cl$, crystallises from alcohol in yellowish-green, and from glacial acetic acid in brick-red, crystals, of which the chromate was prepared. By eliminating one amino-group by means of the diazo reaction, monomethylaposafranine (annexed formula) is obtained (compare Kehrman and Wetter, Abstr., 1898, i, 437). It forms a *chromate*, $(C_{19}H_{16}N_3)_2Cr_2O_7$.

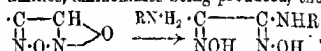
By removing the amino-group from methylaposafranine, or both amino-groups from the original safranin, phenotoluophenazonium is formed. Diazosafranin condenses with β -naphthol to form a blue dye, of which the *chromate*, $(C_{29}H_{22}O_2N_3)_2Cr_2O_7$, was analysed. Z. K.

Synthesis of Safranin with a Naphthalene Nucleus (3:6-Diamino-5-phenyl-2-methylnaphthaphenazonium Chloride). N. N. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 522—530. Compare preceding abstract).—3:6-Diamino-5-phenyl-2-methylnaphthaphenazonium chloride, prepared from naphthaquinonedichlorodi-imide and 4-phenyltolylene-2:4-diamine, forms yellowish-green crystals; the *chromate*, $(C_{23}H_{19}N_4)_2Cr_2O_7$, is described. By eliminating one amino-

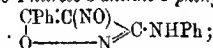
group, the *monoamino*-compound (annexed formula) is obtained, of which the *chromate*, $(C_{23}H_{18}N_3)_2Cr_2O_7$, was analysed. On removing the amino-group, the chromogen *5-phenyl-2-methylnaphthaphenazonium* isolate as the *ferrichloride*, $C_{23}H_{17}N_2Cl_4Fe$, m. p. 205° is obtained. The latter is converted, in ammoniacal solution, into the amino compound. The diazotised naphthasafranin gives a blue dye with β -naphthol, the *chromate*, $(C_{23}H_{24}ON_5)_2Cr_2O_7$, of which was analysed.



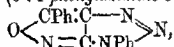
Furoxans. IV. Action of Amines on Dibenzoylfuroxan
 HEINRICH WIELAND and ERWIN GMEIN (*Annalen*, 1910, 375 297—307. Compare Abstr., 1901, i, 609, 610).—The authors' recent work (*loc. cit.*) has shown that the furoxan ring is very easily ruptured by ammonia or amines, amidoximes being produced, thus:



Under suitable conditions the amidoxime may experience ring closure, with the production of *isooxazole* derivatives. These results are utilised to show that Boeseken's benzoyl-*p*-bromoanilinfurazan (this vol., i, 643), obtained by warming diphenyldinitrosoacetyl (di-benzoylfuroxan) with ethereal *p*-bromoaniline, is not a furazan, but a nitrosoisooxazole derivative. Using ethereal aniline (2 mols.), the authors obtain, after the removal of the precipitated benzanilide and evaporation of the solvent, an orange-coloured syrup of the unstable anilino-oxime, $\text{OH} \cdot \text{N} : \text{C} \text{Bz} : \text{C} (\text{N} \cdot \text{OH}) \cdot \text{NHPh}$, which is converted by warm acetic acid into *4-nitroso-3-anilino-5-phenylisooxazole*,



this crystallises in brownish-red needles, and is reduced in alcoholic solution by zinc dust and acetic acid to *4-amino-3-anilino-5-phenylisooxazole*, m. p. 147° (decomp.). An acetic acid solution of the latter is converted by sodium nitrite at 0° into an unstable, red nitrosoamine, $\text{CPh} : \text{C} (\text{NH}_2) \text{---} \text{N} \text{---} \text{C} \cdot \text{NHPh} \cdot \text{NO}$, which rapidly changes to diphenyl-*3:4-gem-triazoloisooxazole* (*3:4-phenylazimino-5-phenylisooxazole*),

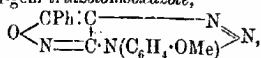


m. p. 151° (decomp.), which crystallises in yellow leaflets, gives a magenta coloration with phenol and sulphuric acid, and develops a dark green coloration with sulphuric acid alone.

When warmed with alcohol or acetic acid, the brownish-red nitrosoanilinophenylisooxazole is converted into the isomeric, colourless azoxime, *3-benzoyl-5-anilino-1:2:4-oxadiazole*, $\text{C} \text{Bz} : \text{N} \text{---} \text{N} \text{---} \text{C} \cdot \text{NHPh}$ (as stated by Boeseken), the formation of which is explained by the intermediate production of the furazan ring, $\text{C} (\text{NHPh}) : \text{N} \text{---} \text{N} \text{---} \text{C} \text{Bz}$.

which then undergoes a partial Beckmann transformation (Böeseken, *loc. cit.*)

[With ALEX. ROSEBU.]—Results similar to the preceding are obtained when dibenzoylfuroxan is decomposed by *p*-anisidine. Nitro-3-*p*-anisidino-5-phenylisooxazole, decomp. 123°, crystallises as glistening, black needles, forms dark red solutions, is converted by boiling alcohol mainly into the isomeric azoxime, and is reduced by lime and acetic acid to 4-amino-3-*p*-anisidino-5-phenylisooxazole, m. p. 51°. This base in acetic acid is converted by sodium nitrite into benzyl-*p*-anisyl-3:4-gem-triazoloisooxazole,



mp. 141°, which crystallises in golden-yellow leaflets.

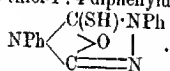
Contrary to Böeseken's statement that dibenzoylfuroxan only reacts with primary amines, the authors find that a vigorous reaction occurs with ethereal piperidine.

C. S.

trazoles. XVII. Rearrangement of the Tautomeric Salts 1:4-Diphenyl-5-thionurazole and 1:4-Diphenyl-5-thiolzole. SIDNEY NIEDLINGER and SALOMON F. ACREE (*Amer. Chem.*, 1910, 44, 219—251).—The slow rearrangement of tautomeric salts and their final states of equilibrium have been investigated by the authors, but the tautomeric salts of such acids have not hitherto been studied. In view of the importance of such work as a test of the validity of Acree's theory, an investigation has now been made of the salts of 1:4-diphenyl-5-thionurazole and 1:4-diphenyl-5-thiolzole.

It has been shown by Busch and Holzmann (*Abstr.*, 1901, i, 234) that Murekwald's thiosemicarbazides (*Abstr.*, 1893, i, 46) are structural isomerides of the types $\text{NH}_2 \cdot \text{NR} \cdot \text{CS} \cdot \text{NHR}$ and $\text{NHR} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHR}$.

The action of carbonyl chloride on $\beta\delta$ -diphenylthiosemicarbazide, a compound, m. p. 141°, is obtained, which was regarded by Busch and Holzmann (*loc. cit.*) as 5-thiol-1:4-diphenylurazole,



but (Abstr., 1902, i, 322) has stated that when this substance is heated, it undergoes transformation into a compound, m. p. 219—221°, which he assumed to be 5-thion-1:4-diphenylurazole, $\text{NPh} \begin{array}{l} \text{CS} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array}$

or a mixture of the two forms in equilibrium, $\text{Ph} \begin{array}{l} \text{CS} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \cdot \text{N} \end{array}$.

It is now shown, however, that these views are incorrect, and that the compound of m. p. 141° is actually 5-thion-1:4-diphenylurazole, which is able of existing in two forms in equilibrium, whilst the compound of m. p. 219—221° is 5-thiol-1:4-diphenylurazole.

The action of diazomethane and diazoethane on 5-thion-1:4-diphenylurazole and 5-thiol-1:4-diphenylurazole, compounds are obtained which differ from those produced by the action of alkyl iodides

M. XCVIII

on the sodium salts of the urazoles. With diazomethane, 5-thion-1:4-diphenylurazole yields a *compound*, $C_{18}H_{12}ON_2S$, m. p. 74.5–75.5; and with diazoethane it furnishes an *ester*, $C_{18}H_{14}ON_2S$, m. p. 79–81°. By the action of diazomethane on 5-thiol-1:4-diphenylurazole, an *ester*, m. p. 129.5–130.5°, is produced, isomeric with that obtained from the thionurazole. The thiolurazole and diazoethane give an *ester*, m. p. 105.5–107.5°.

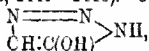
It has been found that 5-thion-1:4-diphenylurazole and 5-thiol-1:4-diphenylurazole yield sodium salts which are reconverted into the respective urazoles on addition of hydrochloric acid. Both salts react with methyl iodide, and the reaction takes place about eighty times as rapidly with the salt of the thiolurazole as with that of the thionurazole. The *methyl ester* of the thionurazole is obtained as a red, viscous oil, which gradually becomes semi-solid. The methyl ester of the thiol compound is identical with that obtained by the action of carbonyl chloride on $\beta\beta$ -diphenyl- γ -methylthiosemicarbazide.

The sodium salts have been esterified quantitatively, and a method has been devised for analysing mixtures of the salts or esters depending on the fact that, under certain conditions, the methyl ester of 5-thiol-1:4-diphenylurazole is completely hydrolysed by alkali hydroxide in presence of chloroform, whilst that of the thionurazole is but little affected by this treatment.

The sodium salts of the two urazoles are mutually convertible into one another by two apparently reversible unimolecular reactions, the velocity of rearrangement of sodium 5-thion-1:4-diphenylurazole being about nine times as great as that of sodium 5-thiol-1:4-diphenylurazole.

E. G.

5-Hydroxy-1:2:3-triazole. THEODOR CURTIUS and AUGUST BOSCHMÜHL (*Ber.*, 1910, 43, 2441–2446).—5-Hydroxy-1:2:3-triazole,



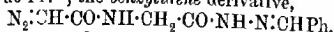
was prepared by Curtius and Thompson (*Abstr.*, 1907, i, 93) from diazoacetamide, and by Dimroth and Aickelin (*Abstr.*, 1907, i, 139) from ethyl-1-phenyl-5-triazolonecarboxylate. It has now been more closely studied (compare Dimroth, this vol., i, 518). 5-Hydroxy-1:2:3-triazole has m. p. 129°; it is a monobasic acid, and forms a colourless crystalline *potassium salt* and a *hydrazonium salt*, $C_3H_2N_3(ON)_2$, crystallising in needles, m. p. 117°. An ammonium salt could not be prepared; on evaporation to dryness with ammonia, a colourless crystalline substance was obtained of the same composition as hydroxy-1:2:3-triazole, m. p. about 95°. On the addition of bromine water to an aqueous solution of 5-hydroxy-1:2:3-triazole, it decomposes, the gas evolved consisting of molecular proportions of nitrogen and carbon monoxide. Probably dibromoglycolic acid (Curtius and Welde, *Abstr.*, 1907, i, 449) is first formed, and decomposes into oxalic acid, which yields carbon monoxide.

E. F. A.

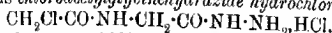
Diazoacetyl-glycinehydrazide and 5-Hydroxy-1:2:3-triazole-1-acetylhydrazide. THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1910, 43, 862–880).—Curtius and Thompson (*Abstr.*, 1906, i, 404, 240;

1907, i. 95) have shown that ethyl diazoacetylglucine yields derivatives of 5-triazolone-1-acetic acid when treated with ammonia or alkali, and the present authors find that hydrazine hydrate reacts similarly with the ester.

Diazoacetylglucinehydrazide, $\text{N}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, prepared by boiling hydrazine hydrate with ethyl diazoacetylglucine (for which an improved method of preparation is given) in alcoholic solution, crystallises in yellow, glistening leaflets, which darken at 120° and decompose at 147° ; the *benzylidene* derivative,



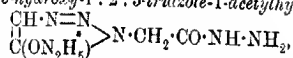
forms minute, almost colourless needles, m. p. $199-200^\circ$, and the *i-propylidene* derivative, $\text{N}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, crystallises in bright yellow, glistening leaflets, m. p. 178° (decomp.). When treated with hydrogen chloride in alcoholic solution, the diazo-hydrazide yields *chloroacetylglucinehydrazide hydrochloride*,



a colourless powder, m. p. 168° ; the *benzylidene* derivative of the base is a colourless powder, which does not melt at 300° .

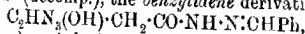
When a cold aqueous solution of diazoacetylglucinehydrazide is treated with a trace of sulphuric acid, nitrogen is evolved, and the solution with benzaldehyde furnishes *hydroxyacetylglucinebenzylidenehydrazide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, crystallising in small, colourless needles, m. p. 143° .

Hydrazonium 5-hydroxy-1:2:3-triazole-1-acetylhydrazide,



is formed as a by-product in the preparation of diazoacetylglucinehydrazide, and is obtained in larger yield by heating ethyl diazoacetylglucine in more concentrated solution with a greater excess of hydrazine hydrate; it forms pale red, feathery crystals, m. p. 175° (decomp.). The *potassium* (m. p. 245° , decomp.) and *silver* (decomp. 209°) salts are described. The *hydrazonium* salt of 5-hydroxytriazole-1-acetic acid, $\text{C}_4\text{HN}_5(\text{ON}_2\text{H}_5)\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{N}_2\text{H}_5$ (reddish needles, m. p. 172°), was also prepared.

5-Hydroxy-1:2:3-triazole-1-acetylhydrazide, $\text{C}_4\text{H}_7\text{O}_2\text{N}_5\cdot\text{H}_2\text{O}$, prepared from the potassium or silver salt, crystallises in colourless, right-angled tablets, m. p. 147° , which are anisotropic; the *hydrochloride*, a colourless powder, m. p. 174° (decomp.), the *benzylidene* derivative,

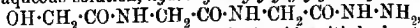


m. p. 190° (decomp.), and the *isopropylidene* derivative, m. p. $155-160^\circ$, were prepared.

J. C. C.

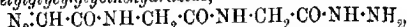
Diazoacetylglucylglucinehydrazide. THEODOR CURTIUS and THOMAS CALLAN (*Ber.*, 1910, 43, 2447-2457).—Curtius and Welde (preceding abstract) have shown that ethyldiazoacetylglucine and hydrazine hydrate yield at first diazoacetylglucinehydrazide, which with a further amount of hydrazine hydrate undergoes rearrangement to the *hydrazonium* salt of 5-hydroxytriazole-1-acetylhydrazide. It is now shown that ethyldiazoacetylglucylglucine forms *diazoacetylglucylglucinehydrazide*. This has the properties of a true diazo compound and also of an acid hydrazide, liberates nitrogen with dilute mineral

acids, and forms a crystalline compound with benzaldehyde. When boiled in aqueous solution, *hydroxyacetylglcylglycinehydrazide*,



is formed. Prolonged boiling of the hydrazide with hydrazine hydrate converts it into a yellow oil, the *hydrazonium* salt of 5-hydroxytriazole-1-acetylglcylglycinehydrazide, the benzylidene derivative of which was obtained crystalline. The triazole derivative is more readily obtained on warming the hydrazide with dilute alcoholic potassium hydroxide, when the *potassium* salt is obtained as a colourless, very hygroscopic substance. The benzylidene derivative of the triazole, as also that of the 5-hydroxytriazole-1-acetylhydrazide of Curtius and Welde (*loc. cit.*), combines with *p*-toluenediazonium sulphate, forming red- and orange-hued azo-dyes respectively.

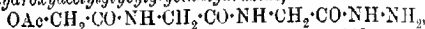
Diazoacetylglcylglycinehydrazide,



crystallises in lustrous, yellow needles, aggregated in rosettes, m. p. 167° (decomp.). *Diazoacetylglcylglycinebenzylidenehydrazide* is a yellow, amorphous powder, m. p. 180—181° (decomp.).

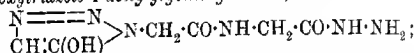
Hydroxyacetylglcylglycinehydrazide is a colourless, very soluble powder, which blackens at 230°, decomp. 240°. *Hydroxyacetylglcylglycinebenzylidenehydrazide* forms short, colourless plates, decomp. 240°.

Acetylhydroxyacetylglcylglycinehydrazide,



is a colourless, microcrystalline powder, decomp. 180°.

5-Hydroxytriazole-1-acetylglcylglycinehydrazide,



the *hydrazonium* salt is a colourless oil, soluble in water with a strongly alkaline reaction; the *potassium* salt is a colourless, crystalline mass.

5-Hydroxytriazole-1-acetylglcylglycinebenzylidenehydrazide is a pale brown, amorphous powder, m. p. 180° (decomp.). It condenses with *p*-toluenediazonium sulphate in dilute sodium hydroxide solution, forming 4-toluenazo-5-hydroxytriazole-1-acetylglcylglycinebenzylidenehydrazide, which crystallises in small, reddish-brown needles, m. p. 151.5°.

4-Toluenazo-5-hydroxytriazole-1-acetylbenzylidenehydrazide forms an orange powder, m. p. 149.5° (decomp.). E. F. A.

Transformation of Diazo-hydrazides into Monohalogen Hydrazides and Azoimides. THEODOR CURTIUS and THOMAS CALLAN (*Ber.*, 1910, 43, 2457—2467).—By the action of gaseous hydrogen chloride on diazoacetylglcylglycinehydrazide, Curtius and Welde (this vol., i, 786) obtained chloroacetylglcylglycinehydrazide hydrochloride. The action of hydrogen bromide and hydrogen iodide has now been studied in a similar manner. The iodine derivative could not be obtained pure, but it condenses with benzaldehyde to form *iodoacetylglcylglycinebenzylidenehydrazide*, $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$. Two other compounds are also formed together with the iodo-derivative, the one, formed in small quantity only, has a high melting point, and is probably the symmetrical secondary hydrazide of iodoacetylglcylglycine. The other, $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_3\text{I}$, crystallises from alcohol in needles; when boiled

with water an ethyl group disappears, and it is supposed that the original compound contains an ethyl group in the hydrazine residue.

When treated with a concentrated aqueous solution of sodium nitrite, the halogen acetylglycinehydrazides are converted into halogen acetylglycineazoimides. These melt and decompose explosively at higher temperatures; they form anilides with aniline, and boiling with alcohol converts them into urethanes.

By the action of hydrogen chloride on diazoacetylglucylglycinehydrazide, a colourless powder, m. p. 172—174°, was obtained, which did not correspond in composition with chloroacetylglucylglycinehydrazide hydrochloride.

Chloroacetylglucineazoimide, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, crystallises from ether in well-formed, colourless, lustrous plates. The aqueous solution when heated desposits a colourless, insoluble powder, m. p. 184—185°.

Chloroacetylglucineanilide forms centimetre-long, colourless needles, m. p. 170—171°.

Chloroacetylaminomethylurethane, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, crystallises in beautiful plates of silky lustre, m. p. 149—150°.

Bromoacetylglucinehydrazide hydrobromide, prepared by the action of hydrogen bromide on diazoacetylglucinehydrazide in alcoholic solution, is a heavy, crystalline powder, deliquescent in the air, decomp. 113°.

Bromoacetylglucinebenzylidenehydrazide is a colourless, amorphous powder, m. p. 187—190° (decomp.).

Bromoacetylglucineazoimide crystallises from ether in colourless, silky, lustrous plates. It melts and explodes when heated on a spatula.

Bromoacetylglucineanilide crystallises in bunches of intergrown, small needles, m. p. 161—162°.

Bromoacetylaminomethylurethane separates from alcohol in colourless plates, m. p. 154—155°.

Iodoacetylglucinebenzylidenehydrazide was obtained as an almost colourless, amorphous powder, m. p. 177—179°.

Iodoacetylglucineazoimide forms colourless platelets, which melt and explode.

Iodoacetylaminomethylurethane crystallises in well-formed, colourless plates, m. p. 171° (decomp.).

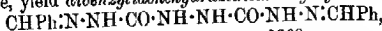
Iodoacetylglucine-ethylhydrazide (?) was obtained in colourless, microscopic needles, m. p. 147—148°. When boiled with water a residue, m. p. 102—104° (decomp.), remained, which with benzaldehyde formed the above-described iodoacetylglucinebenzylidenehydrazide.

Iodoacetylglucineamide, $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of hydrogen iodide on diazoacetylglucineamide, crystallises in glistening, colourless needles and plates, m. p. 173—175°.

E. F. A.

Hydrazidicarboxylhydrazide. ROBERT STOLLÉ [and, in part, O. H. LEVERKUS and R. KRAUCH] (*Ber.*, 1910, 43, 2468—2470 compare Curtius and Heidenreich, *Abstr.*, 1895, i, 12; 1896, i, 143). On prolonged boiling of ethyl hydrazidicarboxylate with hydrazine

hydrate in alcoholic solution, the hydrazine salt of hydrazidicarboxylamide separates out. The mother liquors, when shaken with benzaldehyde, yield *dibenzylidenhydrazidicarboxylhydrazide*,



crystallising + H_2O in slender plates, m. p. 229° .

Hydrazidicarboxylhydrazide hydrochloride, prepared from the benzylidene compound by heating with hot hydrochloric acid, crystallises in small, glistening prisms, decomp. 203° . The condensation product with anisaldehyde has m. p. 218° , that with salicylaldehyde has m. p. 238° . On heating ethylhydrazidicarboxylate with hydrazine hydrate at 76° and evaporating to dryness in a vacuum, *hydrazidicarboxylhydrazide*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, is obtained in monoclinic prisms, m. p. 196° . It reduces ammoniacal silver nitrate in the cold, and Fehling's solution when warmed. The sulphate (+ H_2O) crystallises in strongly refractive prisms, m. p. 210° (decomp.).

Hydrazidicarboxylazoinide has m. p. 146° , and detonates very violently. With aniline in ethereal solution it forms *hydrazidicarboxylanilide*.

Hydrazidicarboxylethylamide crystallises in plates, m. p. 255° .

Hydrazidicarboxylphenylhydrazide has m. p. 213° (decomp.).

E. F. A.

Stereomeric Azobenzenes. CATHERINE V. GORTNER and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1910, 32, 1294—1296).—Although it is evident from the structural formula of azobenzene that it should be capable of existence in *syn*- and *anti*-modifications, only one form has hitherto been described.

On heating azoxybenzene with iron filings, a distillate was obtained which consisted of a red liquid containing a crystalline substance. On removing the red liquid by means of light petroleum, in which it is readily soluble, a substance, m. p. 237° (corr.), was left in the form of light grey needles, representing about 1% of the azoxybenzene used. This substance was not further investigated.

The deep red solution was washed with cold dilute hydrochloric acid and afterwards with water, and was filtered and left to evaporate. In several cases, only ordinary azobenzene, m. p. 68° , crystallising in prisms, was obtained, but, in other cases, a deep red liquid was left, which furnished a stereoisomeride, m. p. 25° (corr.), crystallising in stellate groups of needles. From a mixture of the two isomerides, that melting at 68° may be removed by crystallisation, the new form being left in the mother liquor. The latter modification is probably *syn*-azobenzene. It has been converted into the form melting at 68° , but the reverse change has not been effected.

E. G.

Chromoisomerism and Homochromoisomerism of Azophenols. ARTHUR HANTZSCH (*Ber.*, 1910, 43, 2512—2516).—Anhydrous α -azophenol is green; β -azophenol is dark red (Willstätter and Benz, *Abstr.*, 1907, i, 566). These chromoisomerides, m. p. 216 — 218° (decomp., corr.), are very similar in physical and chemical properties, like the chromoisomeric nitroanilines (this vol. i, 475). The chromoisomeric α - and β -azophenols each form chrome-

isomeric (yellow, red, and green) alkali salts, which, however, show the same absorption spectra in solution. Also, α - and β -azophenols themselves in solution exhibit the same molecular extinction and the same absorption spectra (the orange tinge of β -azophenol in ether, described by Willstätter, is due to the presence of a little phenylhydrazine). Consequently, the azophenols, and also their salts, form homochromoisomerides in solution. This behaviour, examples of which have hitherto been furnished only by stereoisomerides, is further evidence of the *syn*- and *anti*-configurations of the α - and β -azophenols suggested by Willstätter.

C. S.

The Nitration of Diazonium Compounds. FARBERGER VORM, MEISTER, LUCIUS, & BRÜNING (D.R.-P. 224387).—The nitration of diazonium salts frequently yields nitrophenolic compounds, but if the diazotisation is effected in somewhat concentrated sulphuric acid and the solution (or suspension) subsequently treated with nitric acid, or a nitrating mixture, the corresponding nitrated diazonium salts are produced. α -Naphthylamine-5-sulphonic acid (23 parts) was dissolved in concentrated sulphuric acid (200 parts) and treated with nitrosyl-sulphuric acid (13 parts), dissolved in 50 parts of concentrated sulphuric acid, the mixture stirred, and the temperature maintained at 10 – 20° during several hours; it was then treated with potassium nitrate (11 parts), when the partly separated diazonium compound redissolved, and, on careful dilution, the nitrated product slowly separated in orange-yellow crystals.

F. M. G. M.

The Changes Produced by Urea in the Internal Friction and Electrical Conductivity of Protein Solutions. G. MORUZZI (*Biochem. Zeitsch.*, 1910, 23, 97–105).—The addition of urea to a protein solution in small concentration at first produces a decrease of conductivity, for as a non electrolyte, it lessens the movements of ions. Later, or in the case of greater concentrations within a few minutes, conductivity, rises owing to the formation of ammonia. Ammonia can also be detected by Nessler's reagent. Ammonium cyanate acts in the same way. Protein acts in this way in virtue of its being a pseudo-base. Urea is believed to owe its hæmolytic power, and its capacity to unite with complement, to the liberation of ammonia in fluids which contain protein.

W. D. H.

Action of Alkalis on Protein. III. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1910, 63, 165–169. Compare Abstr., 1909, i, 542).—Gelatin was digested with 0.5*N*-sodium hydroxide solution for seven to nineteen days, then precipitated with tannic acid containing a little sodium chloride (precipitate 1), and the filtrate saturated with sodium chloride (precipitate 2). To remove the sodium chloride from the filtrate, this was precipitated with phosphotungstic acid, the resulting precipitate decomposed with barium hydroxide, and the peptone derivatives precipitated by Kossel's silver nitrate-barium hydroxide method (precipitate 3), and, after removal of silver nitrate, the filtrate was precipitated with phosphotungstic acid, the latter removed, and the filtrate precipitated

with sodium bismuth iodide solution (precipitate 4). The precipitates were removed from each of the four precipitates by making use of acetone solutions, and then the precipitates were hydrolysed with 33 per cent. sulphuric acid. The precipitates before hydrolysis gave glycine, *dl*-ornithine, and *L*-valine. After acid hydrolysis, *dl*-histidine, *dl*-arginine, *D*-lysine, and proline were isolated. The action of alkalis on gelatin is thus similar to its action on clupein. Certain groups of the protein molecule are sensitive to racemisation so long as they are not united as "intraprotein." When the gelatin which has been partly racemised by alkali is subjected to acid hydrolysis, certain groups are racemised and others remain in the active form. The ornithine group especially appears to be readily racemised.

J. J. S.

The Amino-acids Obtainable by the Total Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1910, 63, 477—486).—A general account of the methods adopted and results obtained by the author and others is given. The paper also contains some new details of analytical results, and replies to criticisms.

W. D. H.

The Behaviour of Commercial Egg-albumin to Hydriodic Acid. THEODOR WEYL (*Zeitsch. physiol. Chem.*, 1910, 63, 236—242).—The name *iodalbose* is given to the product obtained by the action of hydriodic acid on egg-albumin; the iodine is firmly held, and the passage of ammonia through an alcoholic solution of *iodalbose* still leaves an iodine containing residuo which differs from *iodalbose* mainly in containing less carbon; it is termed *apoiodalbose*. By treatment with zinc, an iodine-free substance, *radalbose*, is obtained, which resembles the original egg-albumin closely in composition. Elementary analyses are given throughout.

W. D. H.

The Union of Iodine in Iodothyreoglobulin. ADOLF OSWALD (*Arch. exp. Path. Pharm.*, 1910, 63, 263—269. Compare Abstr., 1909, i, 123).—All hydrolytic agencies (boiling with acids or alkalis, action of the enzymes trypsin, erepsin, autolase) split off iodine from iodothyreoglobulin in an ionised condition as soon as the protein molecule is broken up into its final cleavage products. A part of the molecule is easily decomposed in this way, and readily yields up its iodine; another part is more resistant.

W. D. H.

Hordein and Bynin. A Contribution to our Knowledge of the Alcoholic Extracts of Barley and Malt Albumin. WILHELM KRAFT (*Zeitsch. ges. Brauwesen*, 1910, 33, 193—195. Compare Abstr., 1907, i, 666; 1908, i, 69).—An account of experiments on the extraction and reactions of hordein and bynin as obtained from malt and barley meal.

Methods of analysis, by hydrolysis and estimation of the decomposition products, are described, and the results compared with those obtained by Osborne and other workers; the two substances were found to resemble each other very closely, but the great difficulty of obtaining them pure rendered the interpretation of results very difficult.

F. M. G. M.

Thrombin, Antithrombin, and Prothrombin. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1910, 23, 453—473).—Thrombin was prepared by extracting washed fibrin with 8% sodium chloride solution, and then precipitating coagulable protein with chloroform. It is soluble in water, is not coagulated by boiling in neutral solutions, it gives the majority of the protein colour tests, and contains no phosphorus or sulphur. When allowed to remain in solution, especially at a high temperature, it gradually loses its power of coagulating fibrinogen. If putrefaction occurs, its coagulating power is at first increased and then lost. Saline solutions may be boiled without losing completely their coagulating power; dialysed solutions are more rapidly and completely destroyed by high temperatures. It keeps indefinitely when dried. Increasing amounts of thrombin give increasing amounts of fibrin, although in decreasing proportion. The weight of fibrin produced by a given submaximal amount of thrombin is not affected by the time during which the thrombin is allowed to act.

The conclusion drawn is that thrombin is probably not an enzyme. One part of thrombin can convert at least two hundred and fifteen times its weight of fibrinogen into fibrin. In the non-coagulable "peptone plasma" of the dog, it is antithrombin which prevents the action of thrombin. This anti-substance is destroyed at 75—80°, but not at 60°. Dilution with water causes spontaneous coagulation in "peptone plasma"; dilution with normal saline solution has no such effect. Prothrombin can be converted into thrombin in solutions free from calcium salts. One experiment is recorded of intravenous injection of large quantities of thrombin; no result followed.

W. D. H.

New Method for the Preparation of Crystals of Blood Colouring Matter. J. OFFRINGA (*Biochem. Zeitsch.*, 1910, 28, 106—111).—Methods previously employed for the preparation of pure hæmoglobin involve the action of heat, solvents, etc., on the blood. The author believes that these processes are not without influence on the labile hæmoglobin, and in any case crystal formation is very slow. He therefore mixes the corpuscles with kieselguhr, and submits the mass to hydraulic pressure. A fairly concentrated hæmoglobin solution is thus obtained, which, in the case of horse-blood, is frozen solid and centrifuged until again fluid, when a fair crop of crystals is left. The solution from pig's blood required previous concentration in an air current. The purity of the crystals was established by measurement of the extinction coefficients with the spectrophotometer. In each case the ratio 1:59 was obtained, agreeing closely with the Hüfner figure, 1:578, for oxyhæmoglobin.

C. D.

The Refractive Indices of Solutions of Certain Proteins. II. The Paranucléins. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, 8, 287—296. Compare this vol., i, 526).—The collective term paranucléin is applied to an insoluble substance which results from the incomplete peptic hydrolysis of casein, and also to the substance which is formed by high concentrations of pep-in from the synthetic products of complete casein hydrolysis. Additional confirmation of

the view that the substances are identical is obtained by a study of their refractive indices (this vol., i, 526), the value of α being 0.0014.

W. D. H.

Comparative Investigation on the Composition and Cleavage Products of Different Silks. X. Monoamino-acids of the Cocoon of the Italian Silk-worm. GEORG ROOSE. XI. The Monoamino-acids of the Cocoon of the Japanese Silk "Haruko." AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, 68, 273—274, 275—276).—The following table gives the results in percentages with the two kinds of cocoon (freed from "gum") employed, calculated on the ash-free substance.

| | Italian. | Japanese. |
|---------------------|----------|-----------|
| Glycine..... | 33.5 | 35.0 |
| Alanine..... | 20.0 | 22.6 |
| Leucine..... | 0.75 | 0.7 |
| Serine | 1.9 | 0.7 |
| Aspartic acid | 1.0 | 1.0 |
| Glutamic acid | 0.25 | 0.07 |
| Phenylalanine..... | 1.2 | 1.3 |
| Tyrosine ... | 9.0 | 9.7 |
| Proline | 0.8 | 0.7 |

W. D. H.

Partial Hydrolysis of Proteins. II. Fibrin heteroproteose. PRÆBUS A. LEVENE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1910, 8, 269—284).—Heteroproteose was prepared from fibrin by a combination of Kühn's and Pick's methods; it contained C 49.52%; H 6.64%, and N 16.46%, which figures agree very well with Pick's. The results of hydrolysis in parts % are as follows:

| | | | |
|--------------------------|------|---------------------|-------|
| Glutamic acid | 9.51 | Aspartic acid | 4.73 |
| Leucine | 3.05 | Glycine | 0.15 |
| isoLeucine | 2.96 | Tyrosine | 3.43 |
| Valine | 3.54 | Arginine | 6.35 |
| Alanine | 3.39 | Histidine | 1.76 |
| Valine-alanine mixture.. | 1.36 | Lysine..... | 4.80 |
| Proline | 4.27 | Cystine | 4.10 |
| Phenylalanine ... | 2.45 | Ammonia | 1.65 |
| | | Total | 53.05 |

W. D. H.

The Study of Enzymes by means of the Synthetical Polypeptides. ARTHUR H. KOELKER (*J. Biol. Chem.*, 1910, 8, 145—175).—*r*-Alanylglycine can be used with great accuracy for the study of proteolytic enzymes, using the optical method. Solutions of *d*-alanylglycine and of *r*-alanylglycine remain unchanged in solution at 15—20° for thirteen months if toluene is used as a preservative. Buchner's grinding method yields the most active enzymes; precipitation with alcohol cannot be used with advantage in the purification of the active principle. The active principle of yeast which hydrolyses alanylglycine dialyses through parchment. The

solution of the enzyme, freed from most of the solids by dialysis, can be evaporated to dryness and redissolved without impairing its activity. The enzyme is still present after thirteen days' digestion at 37° ; heating to 75° for a few minutes destroys it completely. Sodium chloride has no influence on the rate of hydrolysis; calcium chloride in concentration 0.1% increases, and in concentration 1% inhibits, the hydrolysis.

W. D. H.

Isoelectric Constant of Pepsin. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1910, 28, 1-6).—From electrometric measurements of the changes in the hydrogen-ion concentration which are brought about by the passage of a current through solutions of pepsin containing hydrogen ions in gradually diminishing quantities, the authors have obtained the so-called isoelectric constant of pepsin. This is the hydrogen-ion concentration for which the positive and negative ions of the amphoteric electrolyte are equal, and the sum of the ions has a minimum value. The value found is 5.5×10^{-2} . For hydrogen-ion concentrations greater than this, the pepsin migrates to the cathode, and for smaller concentrations towards the anode. If the acidity is much greater than that corresponding with the isoelectric constant, the same effect is found as in the neighbourhood of the isoelectric point. This is attributed in the case of hydrochloric acid solutions to the formation of undissociated pepsinium chloride in presence of the excess of acid.

H. M. D.

Action of Pepsin and Hydrochloric Acid. EMIL ARDERHALDEN and EUGEN STEINBECK (*Zeitsch. physiol. Chem.*, 1910, 68, 293-311).—Gastric juice and hydrochloric acid of the same strength were allowed to act on peptone from various sources, and the result estimated polarimetrically; no change was produced in times varying from one to 170 hours. In similar experiments on native proteins after treatment with gastric juice or hydrochloric acid alone of the same concentration, no effect was observed in either case by the optical method. When solid, denaturalised protein was employed; hydrochloric acid alone produced little or no effect, but gastric juice caused a rise in rotation. If the solidified protein is placed for a short time in gastric juice, washed, and then placed in distilled water, the water after a time at 37° showed evidence of the presence of peptone by the biuret reaction and the polarimeter.

W. D. H.

The Action of Sodium Fluoride on Pepsin and Trypsin. ALBERT J. J. VANDEVELDE and EDM. POPPE (*Biochem. Zeitsch.*, 1910, 28, 134-137).—Amberg and Loevenhart showed that fluorides retard the action of lipase (*Abstr.*, 1908, i, 235), but in the concentrations used they have no effect on the digestive activity of pepsin and trypsin.

W. D. H.

Leucoprotease and Anti-leucoprotease. C. H. BURTON BRADLEY (*J. Hygiene*, 1910, 10, 209-230).—Lympho-protease is a pepsin-like enzyme associated with mono-nuclear leucocytes. Leucoprotease is a trypsin-like enzyme associated with polynuclear leuco-

cytes, and was in the present experiments obtained from pus cells. Experiments on its rate of action are given. It acts only in neutral or faintly alkaline media. The anti-tryptic action of serum varies in different animals, and in the same animal under different conditions (disease, etc.). In the present experiments, the variation in mammals was slight, and immunisation with leucoprotease caused only a small increase of anti-tryptic activity. Goats were the animals used.

W. D. H.

* The Erepsin of the Cabbage (*Brassica oleracea*). ALICE F. BLOOD (*J. Biol. Chem.*, 1910, 8, 215—226).—An active solution of a vegetable erepsin can be prepared from the cabbage by the ammonium sulphate method; the solution deteriorates very slowly if kept cool. It splits off tryptophan from Witte's peptone and from casein, and tyrosine from "peptone Roche." It clots milk and liquefies gelatin. It does not digest fibrin, egg white, or edestin in neutral, acid, or alkaline media, or in the presence of hydrocyanic acid. It is active over a considerable range of acidity and alkalinity, but is inhibited by a concentration of hydrogen ions corresponding with the acidity of methyl orange.

W. D. H.

Some Peculiarities of the Proteolytic Activity of Papain. LAFAYETTE B. MENDEL and ALICE F. BLOOD (*J. Biol. Chem.*, 1910, 8, 177—214).—The digestion of Witte's peptone by papain in the presence of the common antiseptics, judged by the tryptophan test, is very slow. Hydrocyanic acid, however, as Vines pointed out, accelerates proteolysis. The same accelerating effect is noticed when other proteins are digested by papain; it also accelerates the clotting of milk and liquefaction of gelatin. Whether there is more than one enzyme in papain is discussed. Hydrogen sulphide also accelerates the digestion. Hydrocyanic acid is provisionally placed with the co-enzymes. Another peculiarity of papain digestion is that digestion proceeds rapidly even after mixtures of the protein and enzyme have been boiled, and plant proteins are rapidly digested at 80°. Spontaneous deterioration occurs rapidly in solutions of papain; egg-white protects papain in some measure. Extracts of *Ascaris*, which are strongly antipeptic and anti-tryptic, exert no inhibition over papain proteolysis.

W. D. H.

Chemical Composition and Formation of Enzymes. II. HANS EULER and BETH AF UGGLAS (*Arkiv. Kem. Min. Geol.*, 1910, 3, No. 34, 1—12. Compare this vol., i, 345).—I. *Variation of Enzyme Content of Brewer's Yeast*.—No difference was found in the amount of invertase extracted from yeast dried (1) by treatment with absolute alcohol, (2) by treatment with 95% alcohol, (3) by drying in a vacuum at 40°, and (4) dried at 40° and subsequently slowly heated up to 80°. Yeast cultivated for several generations on dextrose-peptone contained about half as much invertase as the same yeast cultivated in sucrose-peptone. A yeast kept some days under toluene water and subsequently dried, had a low inverting power; the same yeast kept in yeast water and 0.5% sucrose, and strongly aerated, had a normal inverting power.

The diastatic power of barley corns germinated in the one case on moist sand, and in the other on sand moistened with $N/10$ -disodium phosphate solution, was in the ratio 1:2:3. The increase is attributed to the formation of a co-enzyme from the absorbed phosphate.

II. *Adsorption of Nitrogenous Substances*.—Iron and aluminium hydroxides adsorb proteins, but are not suited for the separation of protein and peptone. Charcoal entirely adsorbs peptone from solution, whilst from yeast extract it adsorbs both nitrogenous and nitrogen-free compounds. From erythrodextrin solutions about 90% is adsorbed by charcoal. Pectic acid is hardly adsorbed by kaolin, strongly by charcoal. Kaolin adsorbs the carbohydrates from yeast-extract preferentially to the nitrogen compounds. The peptones may be removed by charcoal, but the larger part of the nitrogenous constituents still remains.

E. F. A.

Inversion of Sucrose by Invertase. V. Destruction of Invertase by Acids, Alkalis, and Hot Water. C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1910, 32, 985—989).—It has been shown in an earlier paper (this vol., i, 601) that invertase is destroyed by both acids and alkalis at 30° ; in each case, the destruction begins at a concentration of about $0.01N$, and becomes almost instantaneous at about $0.05N$. It is now found that as the temperature is raised, the rate of destruction by acids and alkalis increases, and that at about 60° water itself slowly destroys the enzyme, and at 65° the destruction is quite rapid. The destruction of invertase by hot water is evidently due to the same cause as its destruction by acids and alkalis, namely, the hydrolysis of the complex enzyme molecule. The rates of destruction in the same medium at different temperatures are compared, and the coefficients of the rates of increase for 10° rise of temperature are recorded. The average value of this coefficient is 3.1, which agrees with the general observation that this factor for most chemical reactions is between 2 and 4. The hydrolytic destruction of invertase by acids, alkalis, and hot water thus accords with the common types of chemical reactions.

It is shown that levulose has a remarkable power of protecting invertase from destruction. The rate of destruction by $0.04N$ -hydrochloric acid, $0.03N$ -sodium hydroxide, 50% alcohol, and hot water was first determined in the absence of the sugar and then with it present in concentrations of 2.7, 5.4, and 10.9%. The results are tabulated and plotted as a curve. This protective action of levulose can be best explained by assuming that the enzyme forms a compound with the sugar which is more resistant to the action of acids, alkalis, hot water, and alcohol than is invertase itself.

E. G.

Inversion of Sucrose by Invertase. VI. Theory of the Influence of Acids and Alkalis on the Activity of Invertase. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1910, 32, 1220—1232).—It has been shown in earlier papers (this vol., i, 601; preceding abstract) that invertase is inactive in alkaline solutions, whilst in presence of dilute acids the activity rises to a maximum and afterwards decreases

with increasing acidity. These phenomena are most readily explained on the assumption that acids and alkalis combine with invertase in accordance with the law of mass-action, and thus prevent it from effecting the inversion of sucrose. On this hypothesis, a formula has been deduced by means of which the activity of invertase has been calculated over a considerable range of acidity and alkalinity. The results thus obtained agree closely with the observed activities.

E. G.

Inversion of Sucrose by Invertase. VII. Effect of Alcohol on Invertase. C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1910, 32, 1350—1357).—The work described in this paper was carried out with the object of ascertaining the influence of alcohol of various concentrations on invertase at 30°. The observation of O'Sullivan and Tompson (*Trans.*, 1890, 77, 927), that the activity of invertase is reduced by alcohol, is confirmed, and it is found that the relation between the strength of the alcohol and the activity of the enzyme may be represented as a logarithmic or hyperbolic function.

Invertase is destroyed by alcohol of certain strengths. The destruction follows the course of unimolecular reactions; it is not appreciable if the alcohol is under 20%, is almost instantaneous at 50%, and then decreases to nearly zero at 80%. The rate of destruction is greatly retarded by the presence of sucrose, 6% of the sugar reducing the rate in 50% alcohol to about 1% of its original value. An equation is given expressing the rate of inversion of sucrose by invertase in presence of sufficient alcohol to effect the slow destruction of the enzyme, and is found to yield results agreeing closely with those obtained by experiment. In this way the activity of invertase has been determined in 50% and 60% alcohol.

Invertase can be precipitated by alcohol of about 90% strength without much being destroyed, and a preparation has been thus obtained with 78% of the activity of the original solution. In presence of sucrose very little invertase is destroyed, even when precipitated with 70% alcohol; by this method the enzyme has been recovered with 94—96% of the original activity.

E. G.

The Invertase of Malt Extracts. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1910, 28, 131—133).—The extract of green malt inverts sucrose. Illustrative experiments are given. W. D. H.

Existence of a Specific Methylglucase in Beer Yeast. BRESSON (*Compt. rend.*, 1910, 151, 485—487. Compare Bierry, *Abstr.*, 1909, ii, 747).—Top-fermentation yeast hydrolyses α -methylglucose, whilst bottom-fermentation yeast does not. The author considers that an extract of the former contains a specific diastase not identical with invertin or maltase.

W. O. W.

Preparation of the Polypeptolytic Ferment of Yeast. A. H. KOELKER (*Zeitsch. physiol. Chem.*, 1910, 67, 297—303).—Whilst the filtered liquid obtained from yeast after treatment with chloro-

form very rapidly causes the hydrolysis of sucrose, it was found that alanylglycine is very slowly hydrolysed by the liquid, which is distinctly acid. When, however, calcium carbonate is added, much carbon dioxide is given off, and the liquid becomes very active, far more so than freshly-prepared expressed yeast.

The liquid is prepared by intimately mixing yeast (500 grams) and precipitated calcium carbonate (30 grams) and adding chloroform (50 c.c.). The yeast liquefies in one to three hours, and is then left for three to four days at the ordinary temperature and filtered. After treating with toluene, it is kept at 38° for auto-digestion until the rotatory power becomes constant (ten to forty hours). When filtered it is ready for use.

Calcium chloride does not increase the hydrolytic activity.

N. H. J. M.

Amylase (Diastase). ALFRED WOHL and E. GLIMM (*Biochem. Zeitsch.*, 1910, 27, 349—375).—The results of experiments on the effect of maltose and other sugars in checking the production of sugar from starch by amylase showed that the union of sugar with the enzyme increases with the concentration of the solution, and is sufficiently complete in 15% maltose solutions to render the production of sugar inappreciable. Similar results were obtained with 10% dextrose solutions, whilst 15% dextrin solution only reduced the activity of amylase to 25%. Galactose (20%) reduced the action by only one-third, and mannose (10%) by only 15%, whilst sucrose and laevulose had no effect.

Addition of 10% of maltose to solutions of amylase enables the latter to retain its enzymatic power when heated at 60° for ten minutes. The same effect is obtained by addition of 20% of dextrose, invert-sugar, and dextrin, whilst sucrose and starch have less effect. In each case the protective action depends on the concentration, and not on the absolute amount of the substance added.

N. H. J. M.

Amylases. II. Action of Pancreatic Amylase. E. C. KENDALL and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1910, 32, 1087—1105. Compare this vol., ii, 1011).—A study of the effect of electrolytes and of the concentration of starch on the amylolytic activity of pancreatin. The best commercial preparations are without action on pure starch, but are activated by the addition of neutral electrolytes, or, better, by the action of both a salt and alkali. Below the concentration for maximum activation, the optimum concentrations of salt and alkali depend on each other; above this concentration the optimum for the alkali depends chiefly on the concentration of the starch. Under these conditions, the initial rate of hydrolysis is independent of the amount of starch, but the rate diminishes as the reaction proceeds, the less rapidly the greater the amount of starch present. Equilibrium is attained in 1% starch solutions when the weight of maltose is about 85% of the initial weight of starch. Between 20° and 40°, the temperature-coefficient for amylase conforms to van't Hoff's rule for normal chemical reactions.

Apart from its action as an alkali, asparagine has little effect as an activating agent.
W. O. W.

Individuality of Cellase and Emulsin. GABRIEL BERTRAND and A. COMPTON (*Compt. rend.*, 1910, 151, 402—404. Compare this vol., i, 212, 220).—Previous experiments not having definitely established the non-identity of cellase and emulsin, a number of comparative observations have been made on the diastases extracted from almonds, maize, and bran. In each case the material was allowed to act on cellose and on amygdalin, when it was found that the ratio between the rates at which these substances underwent hydrolysis varied very considerably according to the source of the enzymes. It would appear, therefore, that cellase and emulsin are two specific enzymes occurring together in plants in variable proportions.
W. O. W.

δ -Emulsin. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, 28, 408—412. Compare this vol., i, 403).—The action of emulsin on amygdalin occurs in three stages: in the first, mandelonitrile-glucoside and α -dextrose are formed; in the second, the first-named substance yields mandelonitrile (*d*-benzaldehyde cyanohydrin) and β -dextrose; in the third stage, the first-named substance splits up into benzaldehyde and hydrogen cyanide. The first two stages are hydrolytic, the third is not, and the enzyme responsible for the splitting of the nitrile (oxynitrilase) is distinct from that concerned in hydrolysis (glucosidase). Complete saturation with magnesium sulphate and filtration leads to the appearance in the filtrate of the hydrolytic enzyme only. In precipitation with copper sulphate and half saturation with ammonium sulphate, the filtrate contains both enzymes. The action of oxynitrilase is reversible.
W. D. H.

Lipase Reactions. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1910, 8, 251—264).—When water is present in excess, the hydrolysis of triolein is regularly increased by an increase of lipase; this suggests a mass effect of lipase on the equilibrium of the reaction. A given amount of lipase can under optimum conditions liberate a definite amount of fatty acid from triolein irrespective of the mass of the latter. If more than 50% of water is present, reversion is negligible. Reversion is only appreciable in conditions approaching desiccation. It is possible that lipase, while important in the hydrolysis and absorption of fats, is not important as a factor in their synthesis and storage in the cell.
W. D. H.

Action of Acids in the Enzymic Decomposition of Oil by Castor Oil Seeds. YOSHIO TANAKA (*J. Coll. Eng. Tōkyō*, 1910, 5, 25—42. Compare Armstrong, Abstr., 1906, i, 126).—Castor oil seeds only hydrolyse fats after acid is added. The absolute quantity of the added acid is the important factor, its concentration having no marked influence. The optimum amount of acid required is related to the amount of castor oil seeds alone, and not to the quantity of oil. In the case of mineral and strong organic acids, the optimum quantities

are proportional to their equivalent weights, with weaker organic acids they are larger. The optimum quantity of an acid of the acetic series increases the higher the homologue is; the inhibitory action of an acid when present in excess is greater the lower the homologue.

Lipase is present in castor oil seeds in the form of an insoluble zymogen, which is readily converted by dilute acid into the insoluble enzyme. The added acid does not act by acidifying the medium, but by liberating enzyme from its zymogen. After treating castor oil seeds with acid and completely washing out all the acid and soluble matter with water, a residue was obtained which hydrolysed fatty oils in neutral solution. This proves lipase to be insoluble and active in a neutral medium. It is less active in the presence of free acid, and inactive in an alkaline medium.

E. F. A.

Filtration of Rennet and Pepsin. CASIMIR FUNK and ALBERT NIEMANN (*Zeitsch. physiol. Chem.*, 1910, 68, 263—272).—A complete parallelism between the actions of the two enzymes rennet and pepsin was found; they behaved exactly in the same way in attempts to separate them by Holder's filtration method.

W. D. H.

Inactivation of Rennet by Shaking. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physiol. Chem.*, 1910, 68, 317—343. Compare this vol., i, 83).—A solution of rennet inactivated by shaking recovers its activity after about an hour. The cause of the inactivation is the concentration of the enzyme on the surface of the froth; on remaining quiet, the former condition of things once more obtains. If the froth is removed after shaking, reactivation does not occur in the residual fluid. There is never a complete return of activity, part of the enzyme disappearing; the non-reversible part of the inactivated rennet increases the longer the shaking is continued; this is regarded as an adsorption phenomenon.

W. D. H.

The Milk-curdling and Proteolytic Action of the Gastric Infusion of Ox and Calf and of Natural Gastric Juice. A. RAKORZY (*Zeitsch. physiol. Chem.*, 1910, 68, 421—463).—The milk-curdling enzyme spoken of as chymosin is not identical with pepsin; the former is easily destroyed by incubating at 40° with dilute hydrochloric acid. The two enzymes can also be separated by dialysis, pepsin being almost completely precipitated, whilst the chymosin remains mainly in solution. Chymosin can be extracted from the stomach with water or very dilute hydrochloric acid; a stronger acid then dissolves out the pepsin. The milk-curdling power of gastric juice is due partly to chymosin, partly to pepsin. The amount of the former enzyme lessens with age, so that in the ox the milk-curdling power is due to pepsin alone. Bang's parachymosin is possibly identical with pepsin.

W. D. H.

Theory of the Action of Oxydases. ALEXIS BACH (*Arch. Sci. phys. nat.*, 1910, [iv], 30, 152—164).—A polemical summary of

the rival theories of the action of oxydases of Bertrand and of Bach. Colloidal aluminium hydroxide and, to a less extent, other aluminium salts accelerate the transformation of the red oxidation product, produced by the action of tyrosinase on tyrosine, into black melanin. Laccase acting on pyrogallol produces a yellow coloration; the solution in time becomes reddish-brown, and deposits crystals of purpurogallin. The addition of a few drops of a solution of an aluminium salt at the yellow stage greatly facilitates the formation of purpurogallin, and the rate of oxidation is the same in a portion of the solution which was boiled to destroy the oxydase. The influence of metallic salts on oxydases is analogous to that of ferrous sulphate on peroxides; the salts are only enabled to act because the oxydase has formed a peroxide. Inorganic salts are not an integral part of oxydases, and do not constitute their active principle; their function is solely to accelerate the oxidising action of the peroxides formed by the true oxydases.

E. F. A.

Peroxydase Character of Oxyhæmoglobin. JULES WOLFF and E. DE STOEKLIN (*Compt. rend.*, 1910, 151, 483—485. Compare Abstr., 1908, i, 490, 573, ii, 1022; 1909, i, 347).—The authors have indicated previously the resemblance between certain colloidal compounds of iron and the peroxydases of vegetable origin. Oxyhæmoglobin is now shown to share this similarity, and it has been found by quantitative experiments on the oxidation of potassium iodide, in the presence of hydrogen peroxide, that its catalytic activity surpasses that of the plant peroxydases. It is extremely sensitive to the influence of other substances in the medium, and loses its activity when the solution is boiled. The best results were obtained in an N/20 solution of sodium citrate; small quantities of organic acids inhibit the action.

Oxyhæmoglobin shows the usual reactions with pyrogallol, guaiacol, and quinol. The substance appears to be more active after a second crystallisation than after the first.

W. O. W.

Isomerisation of Some Phosphorus Compounds. I. ALEXANDER E. ARKUSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 395—420).—The esters of phosphoric acid of the type $P(OR)_3$ under the catalytic influence of alkyl halides are capable of being isomerised into the ethers of the type $PRO(OR)_2$. A rise in temperature of 10° doubles the velocity of reaction, which is also greatest with alkyl iodides and least with the chlorides.

Ethers of the general formulæ $PR'(OR)_2$ and $PR_2'OR$ (where R is an aliphatic radicle, and R' any other aliphatic or aromatic radicle) also undergo isomerisation when treated with alkyl halides, being converted into derivatives of quinquevalent phosphorus, $PRR'OOR$ and $O.PRR_2'$ respectively. The velocity of isomerisation is proportional to the mass or concentration of the catalyst, and to the readiness with which the reacting substance forms intermediate additive products; thus the following is the order of the velocity of isomerisation of some of the substances employed: $PR_2'OEt$, $PR'(OEt)_2$, $P(OEt)_3$.

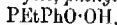
Phenyl chloride, PPhCl_2 , was prepared by a modification of Michaelis' method (this Journ., 1873, 1148; 1874, 168), a detailed description and figure of the modified apparatus being given; when this substance is heated in a sealed tube at 300° , diphenylphosphoryl chloride, Ph_2PCl , is obtained, which, on treatment in ethereal solution with sodium ethoxide, furnishes *ethyl diphenylphosphinite*, $\text{PPh}_2\cdot\text{OEt}$, b. p. $179^\circ/14$ mm., D_4^{20} 1.0896; the *additive product* with copper iodide has m. p. $190-191^\circ$. As a by-product in the formation of the ester, diphenylphosphinic acid, $\text{PPh}_2\cdot\text{O}\cdot\text{OH}$, is obtained. Under the catalytic influence of ethyl iodide at the ordinary temperature, the ester is converted quantitatively into diphenylethylphosphine oxide, $\text{O}\cdot\text{P}(\text{Et})\text{Ph}_2$.

Isopropyl diphenylphosphinite, $\text{PPh}_2\cdot\text{OPr}^i$, has b. p. $160^\circ/8$ mm., D_4^{20} 1.0925, and forms a crystalline *additive* compound with copper iodide, m. p. $114-115^\circ$. *Isopropyl diphenylphosphinate*, $\text{PPh}_2\cdot\text{O}\cdot\text{OPr}^i$, m. p. $95-96^\circ$, is formed as by-product in the preparation of the ester.

On heating at 115° with isopropyl iodide, isopropyl diphenylphosphinite is quantitatively isomerised into *diphenyl isopropylphosphine oxide*, $\text{O}\cdot\text{P}(\text{Pr}^i)\text{Ph}_2$, which crystallises in prisms, m. p. $145-146^\circ$.

Isobutyl diphenylphosphinite, $\text{PPh}_2\cdot\text{OC}_4\text{H}_9$, has b. p. $202-203^\circ/11$ mm., D_4^{20} 1.0311, and forms a crystalline *additive* compound with copper iodide. In the preparation of the ester, *isobutyl diphenylphosphinate*, $\text{PPh}_2\cdot\text{O}\cdot\text{OC}_4\text{H}_9$, m. p. 77° , and diphenylphosphinic acid are also obtained. *Isobutyl diphenylphosphinite*, when heated at 120° with isobutyl iodide, is isomerised to *diphenylisobutylphosphine oxide*, $\text{O}\cdot\text{P}(\text{H}_2\text{C}\cdot\text{C}_3\text{H}_7)\text{Ph}_2$, which forms needles, m. p. $137.5-138^\circ$.

Diphenylmethylphosphine oxide, $\text{O}\cdot\text{P}(\text{MePh})_2$, prepared from diphenylphosphoryl chloride and sodium methoxide, crystallises in needles, m. p. $109-110^\circ$, and diphenylmethylphosphine is formed as a by-product. The intermediate ester was not obtained, as it isomerises so rapidly. Similarly, *diphenylbenzylphosphine oxide*, m. p. $192-193^\circ$, is obtained from diphenylphosphoryl chloride and sodium benzyloxide. Diethyl phenylphosphinite, $\text{PPh}(\text{OEt})_2$, in contact with ethyl iodide is isomerised into *ethyl phenylethylphosphinate*, $\text{PEtPhO}\cdot\text{OEt}$, b. p. $162-164^\circ/16$ mm. On hydrolysis, *phenylethylphosphinic acid*,



m. p. $79-80^\circ$, is formed, of which the barium and silver salts are described.

Z. K.

Preparation of Amino-derivatives of Hydroxyarylsarsinic Acids and Their Reduction Products. FARBERKE VORM. MEISTER, LEIGES & BRÜNING (D.R.-P. 224953. Compare Abstr., 1909, i, 347).—It is found that the therapeutically active hydroxyarylsarsinic acids can be nitrated, and subsequently reduced to the corresponding amino-compounds having enhanced medicinal value.

Nitrophenolsarsinic acid is prepared by dissolving sodium *p*-hydroxyphenylarsinite (144 parts) in 450 c.c. of concentrated sulphuric acid, and slowly dropping in a mixture of 39 c.c. of nitric acid ($D_{1.4}$) with an equal volume of concentrated sulphuric acid, with continual stirring and at a temperature of 0° ; the mixture is diluted with 1250 c.c. of

water, from which the product separates as a yellow powder. The alkali salts are readily soluble in water, yielding deep yellow solutions.

Aminophenolarsinic acid is prepared by the reduction of the foregoing nitro-compound with either sodium amalgam or sodium hyposulphite; it forms minute prisms or leaflets, which blacken and decompose at about 170° .

Diaminoarsenophenol, a yellow powder, is formed by the energetic reduction of nitrophenolarsinic acid with a large excess of sodium hyposulphite; by oxidation with hydrogen peroxide, it is converted into aminophenolarsinic acid.

Nitro-o-cresolarsinic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}(\text{NO}_2)\cdot\text{AsO}_3\text{H}_2$, prepared from *o*-cresolarsinic acid, is a yellow, crystalline powder, sparingly soluble in cold, readily in hot, water.

Amino-o-cresolarsinic acid is exceedingly soluble in water.

Diaminoarsenocresol, m. p. $165-167^{\circ}$ (decomp.), is sparingly soluble in water and in organic solvents.

Dinitrophenolarsinic acid is prepared by the action of excess of nitric acid (D 1.5) with concentrated sulphuric acid on *p*-hydroxyphenylarsinic acid at a temperature of $15-20^{\circ}$; it forms dark yellow leaflets, sparingly soluble in cold, readily in hot, water.

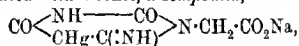
Diaminophenolarsinic acid, silver grey needles, decomposes at about 170° without fusion.

Tetraminoarsenophenol, a bright yellow powder which blackens and decomposes at about $155-157^{\circ}$, is obtained by the reduction of dinitrophenolarsinic acid with a large excess of sodium hyposulphite.

F. M. G. M.

Preparation of Pyrimidine Derivatives containing Mercury.
FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224491).—

When the alkali salt of 4-imino-2:6-diketodihydropyrimidine-3-acetic acid, $\text{CO}\langle\text{NH}-\text{CO}\rangle\text{CH}_2\cdot\text{C}(\text{NH})\rangle\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, is shaken in aqueous suspension with freshly precipitated mercuric oxide or mercury acetamide during several hours, the solution filtered, concentrated in a vacuum, and treated with alcohol, a compound,



is obtained. It is insoluble in organic solvents, but readily soluble in water, and from which mercury is not precipitated on the addition of sodium carbonate.

F. M. G. M.

Organic Chemistry.

Molecular Rearrangements of Carbon Compounds. C. G. DERICK (*J. Amer. Chem. Soc.*, 1910, 32, 1333—1350).—A general paper of a theoretical character, dealing especially with rearrangements of the non reversible type, such as the transformation of Δ^2 -unsaturated acids into their Δ^2 -isomerides. A discussion is given of the formation, stability, and velocity of rearrangement of compounds of this class, and a system of classification of molecular rearrangements of organic compounds is presented. E. G.

Wax Oil. THOR EKECRANTZ and E. LUNDSTRÖM (*Arch. Pharm.*, 1910, 248, 500—513).—At the present time wax oil (*oleum ceræ*) is always prepared by the dry distillation of wax and calcium oxide. The authors have examined wax oil obtained by three different methods: (A) pure beeswax and twice its weight of calcium oxide are distilled in an iron retort, the distillate being rectified by two distillations with twice the quantity of calcium oxide; (B) equal weights of beeswax and calcium oxide are distilled in a glass retort on a sand-bath, the distillate being rectified by a second distillation with an equal weight of calcium oxide; (C) wax oil prepared in an apothecary's laboratory, and guaranteed unadulterated. A is a greyish-yellow mass of crystalline leaflets, and has m. p. 34.5° , D_{20}^{25} 0.792, acid number 15.4, and iodine number 68.3. B is a brownish-yellow oil, having D_{20}^{25} 0.792, acid number 8.7, and iodine number 84.3. C is also a brownish-yellow oil, having D_{20}^{25} 0.790, acid number 9.7, and iodine number 86.6. The oils are distilled with steam, and the residues are separated by acetone into a liquid and a solid portion; from the proportions of the liquid volatile with steam, the liquid non-volatile with steam, and the solid, it is evident that in the distillation of wax and calcium oxide the decomposition of the initially-formed products is least in the oil prepared by method A and greatest in that prepared by method B. The liquid volatile with steam consists chiefly of a mixture of saturated and unsaturated hydrocarbons, containing 10—16 atoms of carbon; the non-volatile liquid, of a similar mixture containing 16—27 atoms of carbon. The solid portion, m. p. $58-59^\circ$, iodine number 13.1, is separated by ether into two parts; one, sparingly soluble in ether, consists chiefly of nonacosane and a little myricyl alcohol; the other, easily soluble in the solvent, is probably a mixture of nonacosane, pentacosane, and a small quantity of unsaturated hydrocarbons. Several commercial wax oils have also been examined. The authors state that the sp. gr. of a wax oil should lie between 0.790 and 0.792, the acid number between 8 and 12, and the iodine number between 80 and 90. They recommend that the iodine number should be determined in the liquid constituents which are volatile with steam. C. S.

Additive Power of 2-Pentene [Δ^2 -Amylene]. ROGER F. BRUNEL and EUGENE G. PROBECK (*Amer. Chem. J.*, 1910, 44, 5, 431—438. Compare Michael, *Abstr.*, 1909, i, 197).—A comparison

is given of the additive power of Δ^{β} -amylenes towards acid with that of β -methyl- Δ^{β} -butylene and of α -butylene. Michael's hypothesis regarding the relation between the position of atoms in a molecule and their influence on each other is adopted (Abstr., 1900, i, 321; 1906, i, 550). According to this hypothesis, if one of the unsaturated carbon atoms in the molecule be numbered 1, the mutual influence between this atom and the other atoms of the molecule will decrease according to the scale: 2—3—5—6—4—7—(9—10—11)—8.

In the case of Δ^{α} -butylene and Δ^{β} -amylenes this gives:



By an additive process the unsaturated atoms in each molecule are compared, and it is shown that from this consideration alone, the greater additive power should be found in the case of Δ^{β} -amylenes, although the difference should not be great. As, however, with the transition from the C_4 to the C_5 series the reduction in the affinity for hydrogen increases, there is a possibility that Δ^{β} -amylenes may show the weaker additive power. This is found experimentally to be the case, the ratio being about 7:5. A similar comparison with β -methyl- Δ^{β} -butylene shows that the difference in additive power in this case must only depend on the degree of attraction of the negative radicals. Experimentally the velocity with which β -methyl- Δ^{β} -butylene dissolves in dilute sulphuric acid is over one hundred times as great as for Δ^{α} -amylenes.

N. C.

The Adsorption of Acetylene by Colloidal Palladium. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1910, 43, 2684—2692).—The liquid hydrosol of palladium, prepared according to the method of Paal and Amberger, dissolves considerable quantities of acetylene. The determination of the amount adsorbed was made in a way similar to that used by Paal and Gerum (Abstr., 1908, ii, 392) to measure the adsorption of hydrogen.

Several days are necessary before the adsorption is complete. After adsorption is complete at room temperature, warming at 40—70°, accompanied by the exercise of a slight pressure, increases the amount of acetylene adsorbed. This extra acetylene is not liberated when the original temperature and pressure are restored, since it is converted partially into volatile and non-volatile condensation and polymerisation products, which, however, could not be isolated in sufficient quantity for identification.

On exposing a palladium hydrosol which has been saturated with acetylene to the air, the chemically unchanged acetylene is set free, especially on warming. On bringing the palladium sol again into contact with acetylene, very little gas is adsorbed, probably because the palladium particles are coated with the acetylene condensation products. This is also the case when the palladium sol is extracted with ether, acidified in order to precipitate the adsorption compound of the solid palladium sol with free protalbic acid, and the precipitate again converted into a liquid sol by the addition of water containing a little sodium hydroxide.

The number of molecules of acetylene adsorbed per gram-atom of

palladium varied from 0.44 to 1.90 molecules, namely, from 1075 to 4630 volumes of acetylene per one volume of palladium, depending on the duration of the experiment and the concentration of the palladium.

T. S. P.

The Adsorption of Acetylene by Palladium Black. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1910, 43, 2692—2694).—The adsorption of acetylene by palladium black was measured in an apparatus similar to that used by Paal and Gerum (*Abstr.*, 1908, ii, 372) to determine the adsorption of hydrogen. The palladium was suspended either in an aqueous solution of sodium protalbate or in an aqueous solution of ammonia, or in aqueous alcohol, in order to determine whether the acetylene adsorbed by the palladium reacted with the dissolved substances. In all three cases, approximately equal quantities of acetylene were adsorbed (1.36—1.53 molecules per gram-atom of palladium); in no case did the adsorption exceed that obtained with colloidal palladium under similar conditions.

Some of the adsorbed acetylene was changed into condensation products, but not to the same extent as with colloidal palladium.

T. S. P.

Tetranitromethane. ERNEST BERGER (*Compt. rend.*, 1910, 151, 812—815. Compare Pictet and Gœuquand, *Abstr.*, 1903, i, 303, 356; Chittaway, *Trans.*, 1910, 97, 2099).—The following method is recommended for the preparation of tetranitromethane. A mixture of 160 grams of absolute nitric acid (or 180 grams of fuming nitric acid) with glacial acetic acid (100 grams) is treated, in a flask kept cool under the tap, with acetic anhydride (290 grams). The flask is allowed to remain in cold water for some hours, and then for a night at the ordinary temperature. After heating for three to four hours at 25—30°, the temperature is raised by 5° every three to four hours until it reaches 65—70°, when the liquid is poured into four times its volume of water. The tetranitromethane is washed and dried over anhydrous sodium sulphate; the acid liquid from which it separates contains trinitromethane and trinitroacetic acid. The yield is 28—60 grams, according to the concentration of the nitric acid.

Tetranitromethane has b. p. 21—23°/22 mm., 124—125°/750 mm. with slight decomposition; D_{20}^{22} 1.620. The heat of combustion was determined in presence of amyl alcohol, since the compound itself contains too much oxygen. The results are expressed by the equations: $C(NO_2)_4 = CO_2 + 2N_2 + 3O_2 + 89.6 \text{ Cal.}$ C diamond + $2N_2(\text{gas}) + 4O_2(\text{gas}) = C(NO_2)_4 + 4.7 \text{ Cal.}$

W. O. W.

Catalytic Reactions by means of Metallic Oxides. ALPHONSE MAILHE (*Chem. Zeit.*, 1910, 43, 1173—1174, 1182—1184, 1201—1204).—In these three papers a résumé is given of the results of recent work carried out by the author and others on the catalytic reactions induced by heated metallic oxides. The first paper deals with the decomposition of alcohols, acids, and esters, and records, for the most part, results already published (Senderens, *Abstr.*, 1907, i, 577; 1908, ii, 166; i, 494, 495; 1909, i, 127, 286, 627; and this vol., i, 11, 179, 318, 489; Sabatier and Mailhe, 1908, i, 594, 713; 1909, i, 546, and this vol., i, 294, 606). In the second paper a theory of these catalyses already outlined (*loc. cit.*, but especially 1908, i, 594, and this vol., i,

294) is discussed in detail in its application to various special cases, and the preparation of amines is described (Abstr., 1909, i, 292), with a number of new examples of the application of the process to this class of compounds. The third paper deals with the preparation and decomposition of thiols by this process (this vol., i, 294, 456, 536).

T. A. H.

Two Active Alcohols and a Third Ketone Contained in Coconut Oil. ALBIN HALLER and A. LASSIZUR (*Compt. rend.*, 1910, 151, 697—699. Compare this vol., i, 355).—The odoriferous constituents of the "essence" of coconut butter have been shown previously to consist of higher fatty acids with neutral substances. The latter have now been separated into alcohols and ketones by means of phthalic anhydride. The alcoholic portion consists chiefly of *d-methylnonylcarbinol*, b. p. 228—233°, D_4^{20} 0.827, n_{20}^{25} 1.4336, $[\alpha]_D^{25}$ +1.24°, with a small quantity of *d-methylheptylcarbinol*, b. p. 195—196°, D_4^{20} 0.823, n_{20}^{25} 1.4249, $[\alpha]_D^{25}$ +2.25°. The ketonic portion contains about 75% of methyl nonyl ketone, together with methyl heptyl ketone and methyl undecyl ketone.

W. O. W.

Basic Properties of Oxygen: Compounds with Bromine and Iodine. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1910, 32, 1330—1333).—It has been suggested by Tschelinzeff and Konowaloff (Abstr., 1909, i, 353) that the compound $C_4H_{10}OBr_2$, obtained by the action of bromine on ethyl ether, has the constitution $C_4H_{10}O \begin{smallmatrix} Br \\ \diagup \\ \diagdown \\ Br \end{smallmatrix}$.

It is now stated that the compound obtained by these authors was not pure, and that the value of the molecular weight in acetic acid which they obtained is not trustworthy, since the dibromide is decomposed by this solvent. Attempts have been made to determine the molecular weight of the di- and tri-bromides of ethyl ether by f. p. measurements in chloroform solution, but without success, since the substance undergoes partial decomposition under those conditions. It has also been found that this constant cannot be determined by Ramsay and Shields' method.

Waentig (this vol., ii, 117) has stated that iodine combines with certain organic solvents at low temperatures. It is now found that when a solution of iodine in alcohol or acetone is cooled to -80° or -90°, a substance separates which may be mistaken for a compound. When completely dried at a low temperature, however, the product is shown by analysis to be iodine, contaminated with a little of the solvent. When ethyl acetate is used, mixed crystals of the solvent and iodine may be obtained.

When bromine and chlorine are dissolved in organic solvents containing oxygen, an appreciable amount of heat is developed, whilst, in the case of iodine, a slight absorption of heat occurs. On the basis of these facts, it is shown that it is improbable that iodine compounds could be produced in a reasonably pure state by cooling the solutions to a low temperature.

E. G.

The Solubilities of the Pharmacopœial Organic Acids and Their Salts. ATHERTON SEIDELL (*Bull. No. 67, Hyg. Lab., U.S. Pub. Health and Mar. Hosp. Serv.*, 1910, 7—98).—The importance attached

to the quotation of solubility determinations in pharmacopœial descriptions of chemicals has led the author to re-determine the solubilities of the organic acids of the United States Pharmacopœia in water, aqueous alcohol, and a number of common organic solvents, and to obtain like data for the official salts of these acids as regards water and aqueous alcohol. The results obtained, together with obviously trustworthy results recorded by previous investigators, are tabulated, and also represented graphically in the original.

The method used consisted in agitating the solvent with excess of the acid or salt at the selected temperature, due precautions being taken to secure saturation in each case and to ensure uniform experimental conditions. The specific gravity of the saturated solution was determined, and then the quantity of substance in solution ascertained by evaporation to dryness, or if this was impossible, by chemical analysis. The results are expressed as the number of grams of substance in 100 grams of the saturated solution.

The following deductions are drawn from a consideration of all the results obtained. Of the thirty-five substances examined, only nine gave results showing satisfactory agreement with the figures quoted in the U. S. P., the remainder showing differences ranging from 5 to 190%. A solubility determination is of little value as a criterion of the purity of a substance. It is impossible to predict the solubility of a substance in a mixture of alcohol and water from a knowledge of its solubility in each of these solvents alone. Citric acid shows nearly parallel solubility curves for the anhydrous and hydrated forms in aqueous alcohol, the second being the more soluble substance. Potassium citrate mixed with aqueous alcohol causes the separation of an upper layer of nearly pure alcohol, and a lower layer of aqueous salt solution (compare Linebarger, Abstr., 1892, 1146). Oleic acid shows apparently unstable solubility equilibrium in aqueous alcohol at certain concentrations. Trichloroacetic acid undergoes partial esterification in aqueous-alcoholic solutions.

T. A. H.

Organic Salts of Yttrium. SEBASTIAN TANATAR and I. VOLZANSKI (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 586—590).—Yttrium propionate, $(EtCO_2)_3Y$, formed by the prolonged heating on a water-bath of yttrium oxide with dilute propionic acid, can be readily obtained pure by recrystallisation. It forms white, monoclinic needles, and is insoluble in all organic solvents except warm alcohol, by which, however, it is converted into the basic salt. The following salts were also obtained: the isobutyrate, $(C_3H_7\cdot CO_2)_3Y$; lactate, $(OH\cdot CHMe\cdot CO_2)_3Y, 4H_2O$; benzoate, $Y(OBz)_3$; fumarate, $(C_4H_3O_3)_3Y, 2H_2O$; phthalate, $(C_8H_4O_4)_3Y, 2C_{10}H_8O_4$; crotonate, $(CHMe\cdot CH\cdot CO_2)_3Y, 5H_2O$; malate, $(C_4H_4O_5)_3Y$; and citronate, $(C_6H_4O_4)_3Y, 9H_2O$.

Yttrium nitrate, $Y(NO_3)_3\cdot 2H_2O$, is formed by dissolving yttrium oxide in excess of dilute nitric acid and evaporating to a syrup, which is dried at 100° . After cooling and stirring, the syrup suddenly forms tiny crystals with development of heat.

Z. K.

Transformation of Stereoisomeric Ethylenic Compounds. I. PAUL PFEIFFER (*Ber.*, 1910, 43, 3039—3048).—When an $\alpha\beta$ -di-haloid derivative of butyric or β -phenylpropionic acid is treated with potassium hydroxide, it furnishes the unstable corresponding α -halogenated *isocrotonic* or *allocinnamic* acid, whereas with pyridine it yields the stable α -halogenated isomeride. In both cases the unstable form is first produced, but in the presence of pyridine this is transformed into its isomeride.

[With A. LANGENBERG].— $\alpha\beta$ -Dichlorobutyric acid reacts slowly with pyridine at the ordinary temperature, but more rapidly on warming at 100°, to give α -chlorocrotonic acid. Under like conditions, $\alpha\beta$ -dibromobutyric acid furnishes α -bromocrotonic acid. $\alpha\beta$ -Dichloro- β -phenylpropionic acid is not decomposed by pyridine at atmospheric temperature, but at 100° furnishes α -chlorocinnamic acid, whilst $\alpha\beta$ -dibromo- β -phenylpropionic acid gives cinnamic with some α -bromocinnamic acid.

α -Chloroisocrotonic acid, when kept in pyridine solution with pyridine hydrochloride at atmospheric temperature, or more rapidly on warming, is converted into α -chlorocrotonic acid, and under like conditions a similar change ensues with α -chloro*allocinnamic* acid, α -bromo*allocinnamic* acid, and α -bromoisocrotonic acid, the last-mentioned acid being also transformed when kept with pyridine alone. β -Chloroisocrotonic acid is not transformed into β -chlorocrotonic acid under these conditions.

T. A. H.

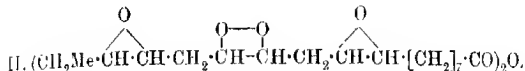
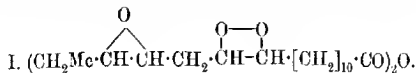
Linolenic Acid and Linseed Oil. ERNST ERDMANN and FRED BEDFORD (*Zeitsch. physiol. Chem.*, 1910, 69, 76—84. Compare Abstr., 1909, i, 357).—Several miscalculations are pointed out in Rollett's work (*Abstr.*, 1909, i, 760). The general conclusions drawn are: (1) The hydrogen and iodine numbers show that in linseed oil there is not more than 20—25% of acids, $C_{18}H_{30}O_2$, containing three ethylene linkings. This is mainly α -linolenic acid, which yields a hexabromide, m. p. 179°. (2) When the solid hexabromide is treated with zinc, a mixture of two stereoisomeric acids is formed; 75% of this mixture consists of β -linolenic acid and 25% of the α -acid. The β -acid yields an oily tetrabromide, and this with zinc gives the β -acid together with polymerisation and anhydro-products. (3) Rollett's conclusions that only one linolenic acid is present in linseed oil, and that the amount is some 50—60%, are incorrect.

J. J. S.

The Composition of Boiled Linseed Oil and the Distribution of Oxygen in Dried Layers of Oil. I. E. I. ONLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 658—676. Compare Erdmann, *Abstr.*, 1909, i, 357).—The solid substances formed when linseed oil is dried on a plate contain unsaturated double linkings, and even when the greatest quantity of oxygen has been absorbed, the dried oil still gives an iodine number not less than 14.15. The amount of oxygen absorbed depends on the thickness of the layer and the surrounding temperature, but in all cases if, after the layer has ceased to increase in weight, the surface of the layer be removed, oxygen commences to be absorbed again and the weight increases.

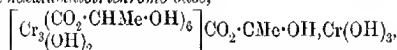
Although fresh linseed oil has no reducing properties, the oil dried on plates is markedly reducing, owing to the formation of two *linoxins* from the glycerides of linolic and linolenic acid.

The *linoxin* (I) from linolenic acid is a solid insoluble in alcohol and ether, that (II) from linolic acid is a soluble syrupy liquid. The *linoxins* are not ozonides, and a detailed study of their properties leads to the conclusion that they have the following constitution :

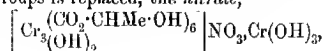


The relative proportions of each formed in various experiments are estimated and found to agree very well with the theoretically calculated numbers. Z. K.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. G. CALCAGNI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 833-337).—By a method analogous to that of Weinland (*Abstr.*, 1909, i, 757), the author has prepared basic salts of hexaglycollato- and hexalactato-trichrome bases. To them is to be assigned a constitution similar to that of the salts obtained by Weinland, so that in this case the alcoholic hydroxyl groups take part in the formation of the salt, whilst other negative radicles (chlorine, bromine) only strengthen the carboxylic hydrogen. The *basic glycollate* of a *hexaglycollatotrichrome base*, $\left[\text{Cr} \left(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{OH} \right)_6 \right] \text{CO}_2 \cdot \text{CH}_2 \cdot \text{OH}, \text{Cr}(\text{OH})_3$, is obtained as a dark green, hygroscopic powder by dissolving chromic hydroxide in glycollic acid and precipitating with alcohol. It is stable towards ammonia and sodium hydroxide; chromic hydroxide is only precipitated after prolonged ebullition with the latter. The *basic lactate* of a *hexalactatotrichrome base*,



was obtained in the same way, and has similar properties. The analytical results indicate the presence of about $5\text{H}_2\text{O}$ in the molecule. When it is treated with fuming nitric acid on the water-bath, only one of the lactate groups is replaced, the *nitrate*,



being formed.

R. V. S.

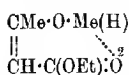
The Equilibrium Isomerism of Acetoacetic Ester and the So-called Isorropesis of its Salts. ARTHUR HANTZSCH (*Ber.*, 1910, 43, 3049-3076).—A systematic investigation of acetoacetic ester and its homologues has been made both by refractometric (compare Brühl, *Abstr.*, 1905, i, 407) and ultra-violet absorption spectra methods, with a view to determining its constitution. The following are the chief results recorded.

The dialkylacetoacetates, which exist only in the ketonic form, absorb but little ultra-violet light, whilst ethyl ethoxycrotonate shows large absorption, but neither of these exhibits much change in absorption in whatever solvent it is examined. Ethyl acetoacetate, on the contrary, shows great variation in absorption, depending on the solvent used; thus, in water and dilute hydrochloric acid, it is slightly absorbent, whilst in indifferent solvents the absorption increases inversely as the dielectric constant of the solvent, and reaches its maximum in hexane. The absorption also increases with rise of temperature and with increasing dilution, the latter especially in hexane. This rise in absorptive capacity is parallel with Brühl's exaltation of refraction. Methyl- and ethyl-acetoacetic esters show similar behaviour. Homogeneous ethyl acetoacetate shows greater absorption than its solutions.

Tables and graphs illustrating these general results are given in the original.

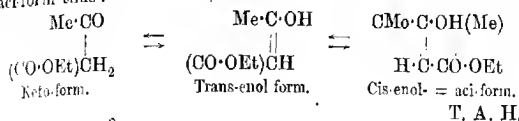
The following explanation of these results is given. The acetoacetates and their mono-substitution products, in the homogeneous state and also in solution in indifferent solvents, are equilibrium mixtures of keto-enolic isomerides. The equilibrium point is shifted to the enol side by (1) rise of temperature, (2) dilution in the same solvent, (3) use of solvents of decreasing dielectric constant. Ethyl acetoacetate is strongly enolised and slightly associated. In dilute hydrochloric acid solution, it is practically entirely ketonised, and in dilute hexane solution almost entirely enolised, since then it shows nearly the same absorption spectrum as ethyl ethoxycrotonate. In water, at medium temperatures, it is about one-fifth, and in methyl alcohol about nine-tenths, enolised. These results are confirmed in part by Stobbe's observations on the ferric chloride test (Abstr., 1907, i, 177).

It is pointed out that the phenomenon of isorropesis (Stewart and Baly, Trans., 1906, 89, 498) is particularly well shown by the addition of alkalis to ethyl acetoacetate (compare Baly and Desch, *ibid.*, 1904, 85, 1036), and is probably the result of "salt" formation, since maximum absorption is reached more quickly the greater the concentration of ester and the more acidie in nature the latter is. Further, the metallic derivatives of ethyl acetoacetate are optically and chemically different from the enol-form of the ester itself, and in these derivatives the ester must exist in a new form, which may be called the aci-form, since it probably also occurs to a minute extent in solutions of the ester in hexane. The relationship of the aci- and enol forms cannot be that of stereoisomerides, as these would be optically identical (this vol., i, 474), and of the formulæ considered for the aci-form, the most likely is the annexed one, the dotted line indicating a "subsidiary valency." This formula represents a "valency isomeride" of the enol form and permits

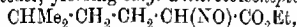


in a modified way of Baly and Desch's "oscillation" explanation of isorropesis, the oscillation taking place by an interchange of "principal" and "subsidiary" linkings at the points marked 1 and 2, with a suitable change in position of the double linkings. Apart from the equilibrium isomerism

between the keto and enol forms and between the enol and aci-forms, there is a third possible equilibrium between the trans-enol and cis-enol forms, and it seems likely that the cis-enol form only can pass into the aci-form thus:



Ethyl α -Nitrosoisheptoate and the Action of Nitrous Gases on Allyl-, Dimethyl-, and Diethyl-acetoacetic Esters. JULIUS SCHMIDT and AUGUST HAID (*Annalen*, 1910, 377, 23–30. Compare Schmidt and Widmann, Abstr., 1909, i, 453).—The nitrous gases from a mixture of nitric acid and arsenious anhydride react with ethyl isheptoate, yielding *ethyl α -nitrosoisheptoate*,



as a dark blue oil, $D_4^{20.2}$ 1.054, and $n_D^{20.2}$ 1.6251. It has a strong odour, cannot be distilled even under very low pressures, and gives Liebermann's nitroso-reaction. When kept or when treated with water or alkalis, the blue liquid becomes colourless; this is partly due to polymerisation, and partly to conversion into the isomeric oximino-derivative. It has a deeper colour, and is also somewhat more stable than the analogous isohexoate (Schmidt and Widmann). When oxidised with hydrogen peroxide, the nitroso-ester yields *ethyl α -nitroisheptoate*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$, as a yellow oil, D_4^{20} 1.070, n_D^{20} 1.4486.

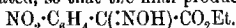
The nitrous gases react with ethyl allylacetacetate, but definite products could not be isolated, and when ethyl dimethyl- and diethyl-acetacetates were used, the unaltered esters were recovered. It would thus appear that substituted acetoacetic esters, in which both the methylene hydrogens are replaced by alkyl groups, cannot yield nitroso-derivatives.

J. J. S.

Esters of Aliphatic Nitroso- and Nitro-carboxylic Acids. JULIUS SCHMIDT and HEDWIG DIETERLE (*Annalen*, 1910, 377, 30–70. Compare Schmidt and Widmann, Abstr., 1909, i, 453; Schmidt and Haid, preceding abstract).—Nitrous gases from arsenious anhydride and nitric acid are able to replace by nitroso-groups, not merely acetyl, but also formyl and benzoyl groups in esters of α -acylated saturated carboxylic acids. The formyl group is replaced most readily, and the benzoyl group least readily. In the last case the reaction requires several days for completion, and the product actually isolated is not a true nitroso-derivative, but the isomeric oximino-compound; at the same time, partial hydrolysis occurs, so that the final product in the case of ethyl benzoylsuccinate is ethyl hydrogen oximinosuccinate, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{Et}$.

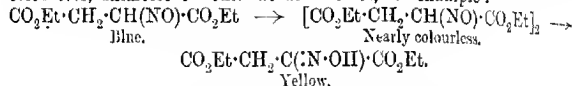
The nitro-group in esters of nitro-substituted saturated acids can also be replaced by the nitroso-group by the action of the nitrous gases on the ester in the absence of a solvent, but it has not been found possible, so far, to replace the bromine atom in α -brominated

esters by the nitroso-group. When ethyl formylphenylacetate is used, an oximino-group replaces the formyl group, and at the same time the phenyl radicle is nitrated, so that the final product is



Ethyl diacetylacetate does not react with the nitrous gases; the presence of a CH-group in the acylated ester is thus essential for the reaction (compare preceding abstract), and it is probable that the nitroso-group first replaces the hydrogen atom of this group and that hydrolysis then takes place, resulting in the elimination of a molecule of the organic acid, for example: $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{NO}) \cdot \text{CO}_2\text{Et} \rightarrow \text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{NO})\text{R} \cdot \text{CO}_2\text{Et} \rightarrow \text{CH}_3 \cdot \text{CO}_2\text{H} + \text{NO} \cdot \text{CHR} \cdot \text{CO}_2\text{Et}.$

The changes which the nitroso-derivatives undergo when kept have been examined, mainly by cryoscopic measurements. In the case of ethyl α -nitrososuccinate and ethyl α -nitroso *n*-butyrate, the blue oils undergo polymerisation, yielding the nearly colourless bimolecular products, which, in their turn, change gradually into the yellow or colourless, unimolecular oximino-derivatives, for example:



In most other cases the second change begins before the first is complete, so that the molecular weight never reaches the value required for the bimolecular compound. This is extremely well shown in the case of ethyl α -nitrosopropionate, prepared from ethyl α -formylpropionate. The conversion into the oximino-compounds is accelerated to an enormous extent by the presence of minute traces of alkalis, and most solvents, for example, water and benzene, also facilitate the transformation.

Good yields of esters of amino-acids cannot be obtained by reducing either the nitroso- or the more stable nitro-esters, the best results being obtained when stannous chloride and hydrochloric acid are used. Small amounts of the oximino-carboxylic acids can be prepared by hydrolysing the esters of the nitroso acids with very dilute alkali at low temperatures. Small yields of the potassium salts of the α -nitro-acids are formed when the corresponding esters are treated with concentrated potassium hydroxide solution. They form golden-yellow crystals, and cannot be transformed into the corresponding acids.

Ebert's ethyl α -oximosuccinate (Abstr., 1885, 1122) is formed readily when ethyl α -nitrososuccinate is shaken with sodium carbonate solution; it has n_D^{20} 1.3765, and when hydrolysed with sodium hydroxide, the oximino-ester yields oximosuccinic acid, ethyl oximinopropionate, or oxalacetic acid, according to the conditions of the experiment, but in all cases the yields are extremely poor, namely, 1 to 2%.

Ethyl α -nitroso *n*-valerate, $\text{CH}_2\text{Et} \cdot \text{CH}(\text{NO}) \cdot \text{CO}_2\text{Et}$, prepared from ethyl *n*-propylacetoacetate, forms a dark blue oil, and retains the blue colour for some twelve to twenty-four hours at the ordinary temperature. It has D_4^{20} 1.213 and n_D^{20} 1.4350, and the isomeric α -oximino-ester is a yellow oil, with n_D^{20} 1.3250. When oxidised with hydrogen peroxide, the nitroso-derivative yields ethyl α -nitro *n*-valerate, $\text{CH}_2\text{Et} \cdot \text{CH}(\text{NO}_2) \cdot \text{CO}_2\text{Et}$, as a yellow oil, with D_4^{20} 1.0551, n_D^{20} 1.4595, and has a very strong odour.

Ethyl α -nitrosohexoate (Abstr., 1909, i, 454) has n_D^{20} 1.4515, and when the corresponding nitro-derivative is treated with concentrated potassium hydroxide solution, yellow crystals of potassium α -nitrohexoate, $C_6H_{11} \cdot CH(NO_2) \cdot CO_2K$, are formed, together with the potassium salt of α -oximinohexoic acid.

α -Oximinohexoic acid, $C_6H_{11} \cdot C(N \cdot OH) \cdot CO_2H$, crystallises from water in colourless needles, m. p. 132° (decomp.).

Pure ethyl α -nitrosopropionate, prepared from ethyl α -formylpropionate, has n_D^{20} 1.4295, and can be kept for two or three days. The best method for transforming it into the isomeric α -oximino-ester is shaking for a few minutes with very dilute sodium hydrogen carbonate solution and keeping for two to three hours.

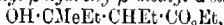
Ethyl oximinonitrophenylacetate, $NO_2 \cdot C_6H_4 \cdot C(N \cdot OH) \cdot CO_2Et$, crystallises from alcohol in colourless, glistening needles, m. p. 195°. It yields sparingly soluble mercurous and silver derivatives, and gives a dirty reddish-brown colour with ferric chloride. The benzoyl derivative, $NO_2 \cdot C_6H_4 \cdot C(CO_2Et) \cdot NO \cdot COPh$, has m. p. 145°, and its methyl ether forms colourless needles, m. p. 151°.

It has not been found possible to isolate a nitroso-derivative from ethyl dibenzoylsuccinate by the action of nitrous gases, although benzoic acid is eliminated.

Ethyl α -benzoylpropionate reacts with nitrous gases, yielding ethyl α -oximinopropionate and the corresponding acid (Ebert, *loc. cit.*).

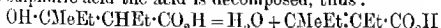
J. J. S.

Synthesis of β -Methyl- $\alpha\beta$ -diethylhydracrylic Acid and its Properties. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 891—899. Compare Abstr., 1909, i, 304).—Ethyl β -methyl- $\alpha\beta$ -diethylhydracrylate [*ethyl β -hydroxy- β -methyl- α -ethylacrylate*],



is best prepared by mixing methyl ethyl ketone with ethyl α -bromobutyrate dissolved in dry benzene, and pouring on to dry zinc previously treated with sulphuric acid. The whole is heated on the water-bath in a reflux apparatus for some hours, after which the product is treated with water, fractionated, and purified. It is a colourless, mobile liquid, b. p. 115.5—116°/25 mm., 214—219°/760 mm. (decomp.), D_4^{20} 0.96230, which with barium hydroxide yields the acid, $OH \cdot CMeEt \cdot CHEt \cdot CO_2H$, of which the potassium, sodium, barium, silver, and copper salts are described.

With sulphuric acid the acid is decomposed, thus:



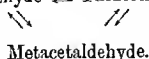
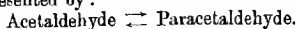
and $OH \cdot CMeEt \cdot CHEt \cdot CO_2H = H_2O + CO_2 + OH \cdot CMeEt \cdot CH_2Et$.

When the ester is treated with phosphoric oxide, ethyl β -methyl- α -ethyl- Δ^2 -pentenoate, $CMeEt \cdot CH_2Et \cdot CO_2Et$, b. p. about 188—190°, is formed, which when treated with potassium hydroxide yields β -methyl- α -ethyl- Δ^2 -pentenoic acid, $CMeEt \cdot CH_2Et \cdot CO_2H$, of which a bromide and the potassium, silver, lead, and calcium salts were prepared.

Z. K.

The Unary Termolecular Pseudo-ternary System: Acetaldehyde, Paracetaldehyde, and Metacetaldehyde. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 318—323).—Observations relating to the connexion between acet-

aldehyde, paracetaldehyde, and metacetaldehyde are discussed, and it is shown that the apparently contradictory results relating to the conditions under which these substances are formed and transformed into one another can be accounted for on the assumption of a ternary equilibrium represented by:



On account of the conversion of metacetaldehyde into the other two isodynamic forms, previous attempts to determine the triple point of metacetaldehyde have given erroneous results. By a method in which the substance, contained in closed thin-walled capillary tubes, was immersed in baths of different temperatures, the melting point of metacetaldehyde under its own vapour pressure was found to be 246.2° . This is much higher than the temperatures, 184° and 167° , obtained by Roozeboom and Hollman respectively. H. M. D.

The System Acetaldehyde-Alcohol. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 329—339).—Experiments have been made to determine the nature of the additive compounds which are formed in mixtures of acetaldehyde and ethyl alcohol. Mixtures which had been kept at the ordinary temperature for about a year, or heated for several hours at 100° , gave no indication of the presence of water when tested with anhydrous copper sulphate. When acetaldehyde-alcohol mixtures are left in contact with copper sulphate for a long time, a blue colour appears, however, and this is supposed to be due to the catalytic influence of the copper salt on the formation of acetal. This accelerating effect affords a convenient method for the preparation of acetal.

The mixing of acetaldehyde and alcohol is attended by a large diminution in volume, and it is found that the density of an equimolar mixture has a maximum value (D_{18}° 0.8719) which is very much greater than that of either of the components. The density data indicate therefore the formation of a compound $\text{CH}_3\cdot\text{COH}\cdot\text{C}_2\text{H}_5\cdot\text{OH}$.

Measurements of the boiling points of various mixtures at different pressures, and of the composition of the vapour emitted by these mixtures, were also made. The curves obtained by plotting boiling points against the composition of the liquid also indicate the formation of the above compound, and a further compound containing a larger proportion of alcohol. Similar conclusions are drawn from the heats of mixing, a maximum heat effect being obtained for an equimolar mixture.

The data obtained in freezing-point measurements confirm these results, and indicate with certainty the formation of compounds, $\text{CH}_3\cdot\text{COH}\cdot\text{C}_2\text{H}_5\cdot\text{OH}$ and $\text{CH}_3\cdot\text{COH}\cdot 2\text{C}_2\text{H}_5\cdot\text{OH}$, which are considerably dissociated at their respective melting points, -122° and -133° . H. M. D.

Preparation of Keten from Acetone. JULIUS SCHMIDLIN and MAXIMILIAN BERGMANN (*Ber.*, 1910, 43, 2821—2823. Compare Wilshire, *Trans.*, 1907, 91, 1938).—Keten appears to be stable

at fairly high temperatures, and a 14% yield can be obtained by passing the vapour of acetone through a hard glass tube filled with porous earthenware and heated at 500—600°. The decomposition of acetone appears to take place in two stages: (1) at about 500—600°, $2\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = 2\text{CH}_3\cdot\text{CO} + 2\text{CH}_4$, and (2) at higher temperatures, $2\text{CH}_3\cdot\text{CO} = 2\text{CO} + \text{C}_2\text{H}_4$. It is impossible to prevent part of the keten from decomposing even at the lower temperature.

It is highly probable that in the preparation of keten from acetic anhydride, acetone is the first product formed. J. J. S.

A New Sugar, Verbascose, from the Root of Mullein. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1910, 151, 760—762*).—A description of the detection and isolation of a new polysaccharide occurring in the roots of *Verbascum thapsus*. The sugar, for which the name *verbascose* is suggested, crystallises in minute, spherular aggregates of slender needles, m. p. 219—220°, on the Maquenne block; $[\alpha]_D + 169.9^\circ$. It appears to be analogous to stachyose, since, on hydrolysis, dextrose, levulose, and galactose are produced. Verbascose does not reduce Fehling's solution; on oxidation with nitric acid, it yields mucic acid.

Verbascum thapsus appears also to contain a glucoside, hydrolysable by emulsin. W. O. W.

Purification of Starch. GIOVANNI MALFITANO and MILE A. N. MOSCHKOFF (*Compt. rend.*, 1910, 151, 817—819. Compare this vol. i, 301).—Further experimental details are given for the preparation of starch free from electrolytes by the method previously described. Potato starch is the variety most amenable to this method of purification. The material so obtained contains less than 0.02% of ash. With hot water it gives a colloidal solution less viscous than an ordinary starch solution, but from which the substance is precipitated by dilution. W. O. W.

The Adsorption of Acids by Carbohydrates. FRED. ROBINSON (*Proc. Camb. Phil. Soc.*, 1910, 15, 548—558. Compare Fenton and Gostling, *Trans.*, 1898, 73, 554).—The dry carbohydrate is covered with chloroform or carbon tetrachloride, a standard solution of dry hydrogen chloride or bromide in the same solvent is then added, and, after several hours, a known volume is withdrawn, shaken with water, and titrated with barium hydroxide.

Carbohydrates adsorb the acids rapidly, the results agreeing well with an exponential adsorption formula, but the relative order of adsorption is not related to the chemical nature of the carbohydrate. It is also independent of chemical action, as the adsorptive power of starch is the greatest, although starch yields the smallest quantity of chloromethylfurfuraldehyde. Lactose and dextrose have the lowest adsorptive power, lactose and maltose differing widely. Levulose and sucrose become pink, and finally black, with hydrogen bromide. C. H. D.

Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1910, 23, 2030—2031).—The conclusions of Jentger (this vol. i, 654) are erroneous, as the cellulose used would retain a considerable quantity of

* and *J. Pharm. Chim.*, 1910, [vii], 2, 481—490.

water, so that the acid is diluted with water, and is not in the so called molecular condition.

C. H. D.

Nitrous Esters of Cellulose. PAUL NICOLARDOT and GEORGES CHERTIER (*Compt. rend.*, 1910, 151, 719—722).—Estimation of the nitrogen in nitrated cellulose by the Schläsing method always gives a higher result than when the analysis is effected in the Lunge nitrometer. This appears to be due to the existence of nitrous esters, which undergo immediate decomposition when dissolved in sulphuric acid. Attempts to prepare such compounds by the action of oxides of nitrogen on cotton under various conditions were unsuccessful, oxidation usually taking place. By their action on viscose, however, in presence of acetic acid, a product was obtained containing 3% of nitrogen (Schläsing) or 5% (Lunge). This was freed from nitrates by treatment with acetone, in which the nitrites are insoluble.

The nitrous esters of cellulose are somewhat unstable, grey substances, pulverulent when dry, but gelatinous when wet. They are insoluble in water and organic solvents; alkalis bring about hydrolysis, nitrites being formed. Hydrolysis is slowly effected by water at the ordinary temperature, and in contact with alcohols, decomposition occurs, the corresponding aldehyde or acid being produced. The deterioration of nitrated cotton is probably connected with the presence of these substances.

W. O. W.

Ammonium and Oxonium Perchlorates. Relationship between Constitution and Behaviour towards Water. KARL A. HOFMANN, R. RÖHN, K. HÜBOLD, and A. METZGER (*Ber.*, 1910, 43, 2624—2630. Compare this vol., i, 105, 168, 187, 370).—The solution of perchlorates in water is primarily due to the formation of hydrates; electrolytic dissociation and hydrolysis are secondary phenomena. Quaternary ammonium perchlorates are not so readily soluble in water as the perchlorates derived from primary, secondary, and tertiary amines. Diazonium perchlorates and the perchlorates of the magenta and methylene-blue series are also sparingly soluble.

Oxonium perchlorates of the type $R_3O \cdot HClO_4$ are readily soluble, whereas tertiary perchlorates, $R_3O \cdot ClO_4$, are sparingly soluble.

These phenomena are attributed to subsidiary valencies of the acidic H atom, which can be used up in attaching water to the molecule of the acid or salt.

The following salts are described: *Trimethylammonium perchlorate*, $NHMe_3 \cdot ClO_4$, doubly refracting prisms and pyramids; at 17° , 20 grams dissolve in 100 of water; *trimethylamineoxazils perchlorate*, $NMe_3O \cdot HClO_4$, hygroscopic cubes; *ethylenediamine perchlorate*, $C_2H_5N_2 \cdot 2HClO_4$, compact prisms, soluble in its own weight of water at 17° ; *tetramethylammonium perchlorate*, $NMe_4 \cdot ClO_4$, tetragonal crystals, decomposing above 300° , solubility 0.341 at 12° , 1.008 at 19° , and 1.554 at 25° ; *tetraethylammonium perchlorate*, solubility 2.392 at 17° , decomposes above 300° ; *trimethylethylammonium perchlorate*, long, rectangular prisms, solubility 11.06 at 17° and 11.97 at 20° ; *trimethylbromoethyl perchlorate*, $C_2H_4Br \cdot NMe_3 \cdot ClO_4$, rectangular plates, m.p. about 200° (decomp.), solubility 3.59 at 19° ; *choline perchlorate*, $OH \cdot C_2H_4 \cdot NMe_3 \cdot ClO_4$, glistening, rectangular plates from absolute

alcohol, solubility 0.89 at 20°; *neurine perchlorate*, $C_8H_9 \cdot NMe_3 \cdot ClO_4$, in prisms, solubility 5.764 at 0°, also soluble in 30% hydrogen peroxide; *betaine perchlorate*, $C_2H_3O_2 \cdot NMe_3 \cdot ClO_4$, doubly refractive plates, solubility 17.73 at 19°; *diphenylhydronium perchlorate*, $IPh_2 \cdot ClO_4$, colourless, felted needles, solubility 0.624 at 19.6°. The perchlorates of malachite-green, crystal-violet, and methylene-blue are sparingly soluble that the solubilities can be estimated by the gravimetric method only. The perchlorates of the corresponding neo-bases are much more readily soluble. *Magenta tetraperchlorate*, $H_2N \cdot N_2 \cdot 4HClO_4$, is a dark orange-coloured, crystalline powder, obtained by mixing the monopерchlorate with 60% perchloric acid and ether; it decomposes above 300° and is hydrolysed by water to the monopерchlorate. *p*-Phenylenediamine, *p*-phenylenedimethylamine, acetyl-*p*-phenylenediamine, and *m*-phenylenediamine, all yield sparingly soluble crystalline diazonium perchlorates, that derived from *p*-phenylenediamine being extremely explosive. The diazo-compounds from *o*-phenylenediamine and *o*- and *p*-aminophenol do not yield crystalline perchlorates.

The following alkaloid perchlorates are formed as precipitates when acetic acid solutions of the base are mixed with excess of 20% perchloric acid solution: *Cinchonine perchlorate* (2), prisms; *strychnine perchlorate* (1), long needles, solubility 0.22 at 15°; *brucine perchlorate* 1, rhombic plates, solubility in 2% perchloric acid solution 0.15 at 18°; *morphine perchlorate* (1), glistening needles, solubility in 4% acid 0.44 at 15°; *cocaine perchlorate* (1), long needles, solubility in 8% acid 0.26 at 6°. The numbers refer to the number of molecules of acid combined with one molecule of alkaloid. Quinine, quinidine, kairine, atropine, nicotine, piperidine, piperazine, and solanine are not precipitated by 20% perchloric acid.

Unisaldehyde perchlorate, $2OMe \cdot C_6H_4 \cdot CHO \cdot HClO_4$, crystallises from etheral solution in colourless prisms or plates, which deliquesce in contact with the air. *Chrysoguinone perchlorate*, $C_{18}H_{10}O_2 \cdot HClO_4$, forms dark violet-coloured prisms, decomposing at about 190°. Anthranol, anthraquinone, diphenylene oxide, and phenyl ether do not yield perchlorates, but dibromophenyl ether and dibromodiphenylene ether yield sparingly soluble perchlorates (3 mols. of oxygen compound to 1 of acid) which are hydrolysed by water.

Xanthoxonium perchlorate, $C_{12}H_9O \cdot ClO_4$, prepared from an ethereal solution of xanthihydrol and 70% perchloric acid, forms intensely yellow crystals; these decompose at 235°, and are hydrolysed by water to xanthihydrol and perchloric acid, but are more stable than the crystals

of xanthone perchlorate. The group $X \cdot O \leq$ is thus comparatively stable (compare Baeyer, this vol., i, 763).

J. J. S.

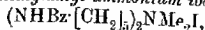
Some Derivatives of Pentamethylenediamine and a New Convenient Synthesis of 2-Methylpyrrolidine from Piperidine. WILHELM VON BRAUN (Ber., 1910, 43, 2864—2879).—2-Methylpyrrolidine, which cannot be obtained from piperidine in the same way that methyldihydroindole is prepared from tetrahydroquinoline, has been synthesised as follows: Benzoylpiperidine is converted by phosphorus

pentachloride into benzoyl- ϵ -chloroamylamine, and this, for practical purposes, is changed by excess of alcoholic sodium iodide into benzoyl- ϵ -iodoamylamine. The latter reacts rapidly with warm alcoholic 33 trimethylamine to form ϵ -benzoylamino-trimethylamylammonium iodide, $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_3\text{I}$, m. p. 189° . (The corresponding chloride is an oil which yields a *platinichloride*, m. p. 198° .) The iodide is converted in the usual manner into a solution of the hydroxide, which, after evaporation to dryness, yields by distillation in a vacuum a mixture of benzoyldimethylpentamethylenediamine, $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$, b. p. $220-225^\circ/10$ mm. (*picrate*, oily; methiodide, m. p. 189° ; see above), and pentenylbenzamide, $\text{CH}_2=\text{CH} \cdot [\text{CH}_2]_3 \cdot \text{NHBz}$, b. p. $195^\circ/13$ mm., which is easily separated, owing to the insolubility of the latter in dilute acids. The solution of the unsaturated compound in concentrated hydrochloric acid, after many hours at 70° , yields on cooling impure benzoyl- δ -chloroamylamine, which is converted by concentrated hydrochloric acid at $150-160^\circ$ into δ -chloroamylamine hydrochloride; this forms a *platinichloride*, m. p. 192° , and is converted into 2-methylpyrrolidine by warming with alkalis. Since the m.p.'s of the *platinichloride* and of the aurichloride, $181-192^\circ$ (decomp.) and 184° respectively, of the 2-methylpyrrolidine thus prepared do not agree with those, $206-207^\circ$ (decomp.) and $158-161^\circ$ respectively, of Tafel and Fenner's 2-methylpyrrolidine, the author's base has been converted by exhaustive methylation into the quaternary methiodide, the *platinichloride* of which, decomp. 255° , blackening at 240° , agrees exactly with the corresponding derivative of Tafel and Fenner's base.

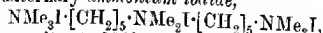
Benzoyldimethylpentamethylenediamine can be readily prepared by heating aqueous dimethylamine (2 mols.) and benzoyl- ϵ -chloroamylamine on the water-bath. By hydrolysis with hydrochloric acid at 150° it yields as *dimethylpentamethylenediamine*, $\text{NMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{NH}_2$, b. p. $181-182^\circ$ (*aurichloride*, m. p. 168°). Benzoyldiethylpentamethylenediamine, $\text{NEt}_2 \cdot [\text{CH}_2]_5 \cdot \text{NHBz}$, b. p. $232-234^\circ/10$ mm., similarly prepared from diethylamine, yields by hydrolysis as *diethylpentamethylenediamine*, h. p. $87-88^\circ/10$ mm. [*platinichloride*, m. p. 215° (decomp.); *picrate*, m. p. 110°]. Benzoyldiisobutylpentamethylenediamine, $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{N}(\text{C}_4\text{H}_9)_2$, b. p. $250^\circ/10$ mm. (decomp.), yields by hydrolysis as *diisobutylpentamethylene-diamine*, b. p. $126-127^\circ/11$ mm. [*platinichloride*, m. p. 212°]. These three *as-dialkylpentamethylene-diamines* are almost odourless, remain unchanged above 200° , are almost unaffected by air, and do not react with nitrous acid. This inactivity is attributed to steric causes, not to a concentration of the basic properties at the tertiary nitrogen atom to such an extent that the primary nitrogen atom no longer exerts basic functions. The latter explanation is rejected because *as-phenylmethylpentamethylene-diamine*, $\text{NH}_2 \cdot [\text{CH}_2]_5 \cdot \text{NPhMe}$, b. p. $180^\circ/16$ mm. (prepared by hydrolysing the benzoyl derivative obtained from methylaniline and benzoyl- ϵ -iodoamylamine), in which the tertiary nitrogen atom probably has a weaker basic function than the primary, reacts with nitrous acid without the evolution of a gas (probably, therefore, a nitroso-group enters the phenyl nucleus), and also because *o- γ -dimethylaminopropylamine*, $\text{NMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, b. p. $151^\circ/15$ mm. [*picrate*, m. p. $173-174^\circ$; *platinichloride*, m. p. 213° (decomp.)], in which the aromatic amino-

group is certainly weaker than the aliphatic dimethylamino-group, reacts with nitrous acid with evolution of nitrogen, forming a substance which is soluble in alkalis and is therefore probably *o*- γ -dimethylaminopropylphenol. *o*- γ -Dimethylaminopropylaniline is obtained by hydrolysing its benzoyl derivative, which is prepared from *o*- γ -chloropropylbenzanilide and dimethylamine.

*Di- ϵ -benzoylamino*dimethylamyl ammonium iodide,



m. p. 162° , obtained as a by-product in the reaction between dimethylamine and benzoyl ϵ -iodoamylamine, is converted by hydriodic acid at 160° into *di- ϵ -aminodimethylamyl ammonium iodide dihydriodide*, $(\text{HI} \cdot \text{NH}_2 \cdot [\text{CH}_2]_5)_2 \text{NMe}_3 \text{I}$, m. p. 210° ; the corresponding *dihydrochloride*, $(\text{HCl} \cdot \text{NH}_2 \cdot [\text{CH}_2]_5)_2 \text{NMe}_3 \text{Cl}$, has m. p. 240° , and forms a *platinichloride*, m. p. 221° . The dihydriodide by exhaustive methylation yields the *tris-quaternary ammonium iodide*,

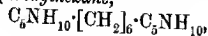


which does not melt at 300° ; the corresponding *tris-quaternary chloride* is extremely hygroscopic, and forms a *platinichloride*, m. p. 286° ; blackening at about 250° .

C. S.

Cyclic Imines. IV. Constitution of Hexamethyleneimine and the Action of $\alpha\zeta$ -Diiodohexane on Bases. JULIUS JOSE BRAUN (*Ber.*, 1910, 43, 2853—2864).—The presence of a seven-membered heterocyclic ring in hexamethyleneimine, which is denied by Blaise and Houillon (*Abstr.*, 1906, i, 692), is proved by distilling *hexamethyleneimine*, b. p. 206 — $208^\circ/19$ mm., with phosphorus pentachloride and boiling the portion of the distillate which is insoluble in water with an excess of alcoholic sodium phenoxide for ten hours, whereby $\alpha\zeta$ -diphenoxyhexane is obtained in 65% yield.

The reactions between $\alpha\zeta$ -diiodohexane and methylamine, dimethylamine, aniline, and piperidine do not yield a trace of hexamethyleneimine derivatives, the products being derivatives of $\alpha\zeta$ -diaminohexane and of α -pipercoline, and substances of high molecular weight. Thus $\alpha\zeta$ -diiodohexane and aqueous methylamine (4 mols.) in the presence of a little alcohol, after two days at the ordinary temperature, yield 6% of 1-methyl-2-pipercoline (identified in the form of the methiodide, m. p. 255°) and the platinichloride, decomp. 222° , obtained therefrom), 3% of dimethyl- $\alpha\zeta$ -diaminohexane (*dibenzenesulphonyl* derivative, m. p. 182° ; *picrate*, m. p. 137°), and about 70% of a mixture of substances of high molecular weight. When heated on the water-bath for many hours, $\alpha\zeta$ -diiodohexane and aniline (3 to 4 mols.) yield, *o*-phenylhexamethyleneimine or phenyl- α -pipercoline, but about 50% of *di*phenyl- $\alpha\zeta$ -diaminohexane, $\text{NHPh} \cdot [\text{CH}_2]_6 \cdot \text{NHPh}$, m. p. 74° , which forms a *picrate*, m. p. 172° , a *dibenzoyl* derivative, m. p. 163° , and a *diazotro*-compound, m. p. 69° . $\alpha\zeta$ -Diiodohexane and dimethylamine yield dimethyl-2-pipercolinium iodide and *tetramethyl- $\alpha\zeta$ -diaminohexane*, $\text{NMe}_3 \cdot [\text{CH}_2]_6 \cdot \text{NMe}_3$, b. p. $103^\circ/20$ mm., which forms a *picrate*, m. p. 162° , and a *methiodide*, which does not melt at 270° . $\alpha\zeta$ -Diiodohexane and piperidine in alcoholic solution on the water-bath yield about 50% of $\alpha\zeta$ -di-1-piperidylhexane,



h. p. 198°/16 mm. (*picrate*, m. p. 208°, blackening at 195°; *platini chloride*, m. p. 230°; *methiodide*, m. p. 240°), together with a quaternary iodide, $\text{CH}_2\langle\text{CH}_2\text{---CH}_2\rangle\text{NI}\langle\text{CHMeCH}_2\rangle\text{CH}_2$, m. p. 263°, which is identical with the product obtained from 2-pipecolide and α -di-iodopentane.

The preceding behaviour of di-iodohexane with primary and secondary bases proves that caution is necessary in assigning cyclic structures to substances produced in reactions in which the reagents employed would, apparently obviously, produce ring compounds.

C. S.

Detection of Choline. Trimethylamine. MAX KAUFFMANN and DANIEL VORLÄNNER (*Ber.*, 1910, 43, 2735—2743).—Choline platini chloride is dimorphous; it separates from water in monoclinic anhydrous crystals, and from dilute alcohol in regular octahedra and cubes or combinations of these. The monoclinic salt is slightly deeper orange in colour; both have m. p. 215—240° with frothing. The monoclinic salt is doubly refractive. The conversion of one form into the other takes place on crystallisation from water or 50% alcohol respectively, and affords a certain test for the presence of choline. Choline may also be detected by distillation with potassium hydroxide, when trimethylamine is formed and recognised by its odour. When trimethylamine is smelt for any length of time, the odour becomes firstly like that of a monoamine, and subsequently like that of ammonia which persists. Many other substances show a similar "reversal of odour."

When choline chloride is heated with excess of benzenesulphonyl chloride, trimethylchloroethylammonium chloride, $\text{NMe}_3(\text{C}_2\text{H}_4\text{Cl})\text{Cl}$, is formed. The platini chloride crystallises in octahedra, m. p. 251°; the *aurichloride* forms slender, yellow, doubly-refractive needles. This chloroethyl base takes a middle position between neurine and choline in its toxic qualities.

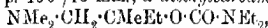
By the interaction of aqueous trimethylamine and benzenesulphonyl chloride, a quaternary ammonium salt is obtained. The *platini chloride*, $(\text{SO}_2\text{Ph}\cdot\text{NMe}_3)_2\text{PtCl}_6\cdot 4\text{H}_2\text{O}$ (?), crystallises in anisotropic, prismatic, or tabular forms, m. p. 209—223°. The *aurichloride* separates in microscopic, doubly-refractive needles, m. p. 196°, decomp. 246°. The *chloride* was obtained in needles; it gives a yellow precipitate with picric acid.

E. F. A.

Derivatives of Amino-alcohols. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1910, [vii], 2, 337—344, 397—401. Compare this vol., i, 246).—The first paper deals with the esterification of these alcohols, and shows (1) that the salts of such esters are easily crystallisable, and are convenient for the identification of the alcohols; (2) that they are readily obtained by mixing solutions in benzene of the amino-alcohols and the necessary acid chloride or bromide, and (3) that this method of formation appears to be analogous with Einhorn's method of using pyridine to promote esterification of alcohols, an additive product of the type $\text{CH}_2\text{R}\cdot\text{N}(\text{CO}\cdot\text{R})\text{R}_2\text{Cl}$ being formed in both cases, which on

warming yields the ester. Mairé's observation that amino-alcohols containing two ethyl groups attached to the nitrogen atom behave abnormally, is confirmed (Abstr., 1908, i, 248), but an ester was obtained in this case by avoiding the use of any solvent. Such amino-alcohols, however, behave normally with cinnamoyl chloride. The esters of the amino-alcohols are liquid, distil without decomposition, are stable towards alkalis, are easily hydrolysed by mineral acids, and are much less basic than the amino-alcohols; they have little or no colour. Their halogen acid salts crystallise well as a rule, but may be hygroscopic. The second paper describes a series of amides obtained by the application of the Schotten-Baumann reaction to the amino-alcohols. In these conditions no esterification of the hydroxyl group occurs.

Dimethylaminotrimethylcarbinol hydrochloride furnishes a *benzoate*, m. p. 202° , crystallising with 1 mol. of alcohol, a *cinnamate*, m. p. 208° , and an *isovalerate*, m. p. 125° . Dimethylaminodimethylethylcarbinol gives a *benzoate*, b. p. $150^{\circ}/13$ mm., a *diethylcarbamate*,



b. p. $136^{\circ}/41$ mm. [the *hydrochloride* of which, m. p. 142° (decomp.), crystallises from acetone in hygroscopic needles, and yields an *aurichloride*, m. p. 98° , which forms orange-red needles, whilst the *hydrobromide*, m. p. 148° , is very soluble in alcohol and exhibits a marked sedative action], a *valerate*, b. p. $128^{\circ}/23$ mm. (yielding a *hydrochloride*, m. p. 151° , and a *hydrobromide*, m. p. 126° , both of which are anaesthetics), a *bromovalerate hydrochloride*, m. p. 158° , which is markedly anaesthetic, a *diethylacetate hydrobromide*, m. p. 169° , a *bromodiethylacetate hydrochloride*, m. p. 160° , a *hexoate*, b. p. 152° (under reduced pressure), a *bromohexoate hydrochloride*, m. p. 130° , a *bromooheptoate hydrochloride*, m. p. 128° (which is markedly anaesthetic), and a *bromolaurate hydrochloride*, m. p. 99° . The higher homologues beyond the hexoate show increasingly the characters of the acid group, and exhibit the properties of soaps. The *hydrochlorides* of the *benzoyl* derivatives of the following amino-alcohols: dimethylaminomethyldiethylcarbinol, dimethylaminodimethylpropylcarbinol, diethylaminodimethylethylcarbinol, and dimethylaminodimethylisocamylcarbinol melt at 180° , 146° , 140° , and 142° respectively. The last of these gives a *platinichloride*, m. p. 178° , and the amino-alcohol also furnishes a *cinnamate hydrochloride*, m. p. 110° .

Aminodimethylethylcarbinol gives with bromovaleryl chloride an *amide*, $\text{CHMe}_2\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$, m. p. 93° , forming brilliant octahedral crystals. Valeryl chloride yields with the same amino-alcohol an *amide*, m. p. $50-60^{\circ}$, b. p. $190^{\circ}/32$ mm., and with methylaminodimethylethylcarbinol and iminobisdimethylethylcarbinol, *amides*, having b. p. $163^{\circ}/25$ mm. and $210^{\circ}/23$ mm. respectively; the second substance crystallises in spangles, and has m. p. $152-153^{\circ}$. All these amides are sedative, and some of them hypnotic; they are less toxic than the corresponding esters described in the first paper.

Ethyl chlorocarbonate reacts in presence of sodium hydrogen carbonate with aminodimethylethylcarbinol to form the *urethane*, $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, b. p. $151-152^{\circ}/17$ mm., whilst with

the same alcohol propyl chlorocarbonate furnishes the *propyl* ester, having b. p. 174—175°. These urethanes are hypnotic in action, but must be given in large doses, for example, 0.4 gram per kilo. of body weight in rabbits. They are toxic to rabbits in doses of 1.8 grams per kilo.

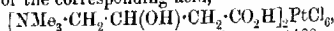
Aminodimethylethylcarbinol with potassium isocyanate yields the substituted *carbamide*, $\text{OH} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, m. p. 156°, which is a powerful hypnotic; the corresponding *methylcarbamide*, similarly obtained, has m. p. 128°, and *carbamide bisdimethylethylcarbinol*, m. p. 96° (approx.).

T. A. H.

Carnitine; Synthesis of γ -Trimethylamino- β -hydroxybutyric Acid. R. ENGELAND (*Ber.*, 1910, 43, 2705—2707).—Carnitine, present in meat extract, has been pronounced to be γ -trimethylamino- α -hydroxybutyric acid (Engeland, *Abstr.*, 1909, i, 557). It is shown now to differ from γ -trimethylamino- β -hydroxybutyric acid, which is obtained synthetically by heating epichlorohydrin with anhydrous hydrogen cyanide to form chlorohydroxybutyronitrile; this, when heated with alcoholic trimethylamine in sealed tubes at 110°, or even in open vessels at 70—80°, is converted into the *chloride* of γ -trimethylamino- β -hydroxybutyronitrile. The *aurichloride* of this compound crystallises in reddish-yellow prisms, m. p. 124—125°. Hydrolysis of the nitrile requires ten hours' boiling with a mixture of aqueous and alcoholic hydrochloric acid. A by-product is a bimolecular anhydride-like product, of which the sparingly soluble *aurichloride*, $\text{C}_{14}\text{H}_{20}\text{O}_5\text{N}_3 \cdot 2\text{AuCl}_4$, was analysed. The *aurichloride* of γ -trimethylamino- β -hydroxybutyric acid crystallises in reddish-yellow plates, m. p. 145°, decomp. at 225°. The *chloride* crystallises in needles, sparingly soluble in alcohol. When heated with alcohol containing hydrogen chloride, it is converted quantitatively into the *ethyl* ester, the *platinichloride* of which sinters at 200°, m. p. 210—212°. These derivatives are very different from those of carnitine.

R. F. A.

Syntheses of Hydroxybetaines. II. Synthesis of γ -Trimethyl- β -hydroxybutyrobetaine (*dl*-isoCarnitine). ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1910, 69, 60—65. Compare this vol., i, 658).—*Ethyl γ -trimethylamino- β -hydroxybutyrate chloride*, $\text{NMe}_3\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is formed when Lespieau's ethyl γ -chloro- β -hydroxybutyrate (*Abstr.*, 1899, i, 243, 790) is heated with an alcoholic solution of trimethylamine for six hours at 100°. The *platinichloride*, $\text{C}_{14}\text{H}_{20}\text{O}_5\text{N}_3\text{PtCl}_6$, crystallises from 90% alcohol in slender, pale yellow needles, which decompose at 233—234°. The *platinichloride* of the corresponding acid,



forms orange-coloured crystals, decomposing at 248°, and is isomeric with carnitine platinichloride (m. p. 214—218°).

A by-product obtained in the preparation of the ester is trimethyl-ethylammonium chloride, which is deposited as the *platinichloride*, $(\text{NMe}_3\text{Et})_2\text{PtCl}_6$, in the form of pale orange-coloured plates decomposing at 281—284°. The corresponding *aurichloride*, $\text{NMe}_3\text{EtCl}_4\text{AuCl}_4$, forms characteristic needles, which are unchanged at 290°. J. J. S.

Action of Ammonia on Unsaturated Acids. II. GEORGE I. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 885—890. Compare Abstr., 1909, i, 772).—In order to confirm the explanation already given for the formation of imino-acids by the action of aqueous ammonia on unsaturated acids, a mixture of crotonic and aminoacetic acids was heated in a sealed tube at 120—130° with sufficient aqueous ammonia to convert both acids into their ammonium salts. The products of the reaction were ethyl β -aminobutyrate and diethyl- β -iminobutyrateacetate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b. p. 144° 19 mm., D_4^{20} 1.0340, n_D^{20} 1.4370, a colourless, mobile liquid, soluble in alcohol and ether, and readily saponified into β -iminoacetic-butyric acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 200° (decomp.). To avoid the formation of β -amino-acid, and thus make this a convenient general method for the preparation of imino-acids, the ammonium salts are substituted by the potassium salts of the amino- and unsaturated acids. To prove that glycine unites with crotonic acid in the β -position, propaldehyde and potassium cyanide were made to react with the hydrochloride of ethyl aminoacetate, when α -iminoacetic-butyric acid, $\text{CO}_2\text{H}\cdot\text{CHEt}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, H_2O , was formed. It forms large, elongated prisms, m. p. 104—105°. The hydrochloride forms small crystals, decomposing at 175—177°. Thus, in the interaction of α -amino-acids with crotonic acid, $\alpha\beta$ -imino-dialiphatic acids are formed. Z. K.

Synthesis of γ -Guanidinobutyric Acid. R. ENGELAND and FR. KUTSCHER (*Ber.*, 1910, 43, 2882—2883).—This substance may be readily prepared by the following method. Concentrated solutions of cyanamide and of twice its weight of γ -aminobutyric acid are mixed, rendered alkaline with a few drops of ammonia, and kept for five weeks at the ordinary temperature, the evaporated ammonia being replaced from time to time. The guanidinobutyric acid which crystallises out is purified by conversion into the hydrochloride, which is sparingly soluble in concentrated hydrochloric acid and in alcohol. The aurichloride, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2\text{AuCl}_4$, forms broad, lustrous plates, m. p. 198—200°. The hydrochloride regenerated from it has m. p. 184°; it is precipitated by phosphotungstic acid even from dilute solutions, but not by picric acid or sodium picrate. The synthetic acid is identical with that obtained by oxidation of arginine or agmatine.

R. V. S.

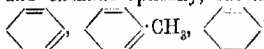
Action of Some Salts of Tervalent Metals on Thiocyanates. CORRADO BONGIOVANNI (*Boll. chim. farm.*, 1910, 49, 789—791. Compare Abstr., 1908, i, 859).—Molybdenum thiocyanate is decolorised by the same substances which decolorise ferric thiocyanate. Chromic hydroxide and thiocyanic acid yield a reddish-violet solution, which is much less intensely coloured than that of ferric thiocyanate, and it behaves differently in other respects, for it is not hydrolysed appreciably, and is not decolorised by saline solutions, oxalic acid, or acetic acid. Vanadium thiocyanate behaves similarly to the ferric compound. The mode of formation and the properties of these substances do not accord with Tarugi's hypothesis (*loc. cit.*) as to their constitution.

R. V. S.

Orientation in the Benzene Nucleus. JULIUS OBERMILLER (*J. pr. Chem.*, 1910, [ii], 82, 462—472).—A reply to, and a claim for priority over, Holleman.

C. S.

Unsaturated Hydroaromatic Hydrocarbons with Semicyclic Double Linkings. KARL AUWERS and G. PETERS (*Ber.*, 1910, 43, 3076—3094).—In two papers published already (this vol., ii, 365, 367), Auwers and Eisenlühr discuss the determination of constitution by optical methods, and point out the importance of ascertaining the normal value of the exaltation of refractivity and dispersivity in undisturbed conjugated systems and the influence thereon of various kinds of distortion. In pursuance of this object they are attempting to prepare and examine optically, substances derived from the three systems



and the present paper gives the results of attempts to solve this question for the third of these

1:3-Dimethyl- Δ^3 -cyclohexen-5-one on treatment with magnesium methyl iodide furnishes 1:3:5-trimethyl- Δ^3 -cyclohexen-5-ol, m. p. 46°, b. p. 87—90°/17 mm., D_4^{20} 0.9132 to 0.9140, n_D^{20} 1.47349, $n_D^{19.3}$ 1.47053, and $n_D^{18.3}$ 1.48715 (whence $\Sigma_s = +0.36$, $\Sigma_D = +0.34$, and $\Sigma_v - \Sigma_s = 9\%$); it is crystalline. On heating alone or with dehydrating agents, it yields a hydrocarbon having b. p. 63—64°/17 mm. or 151°/760 mm., D_4^{20} 0.821 to 0.828, n_D^{20} 1.467 to 1.477, n_D^{19} 1.471 to 1.481 (whence $\Sigma_s = +0.68$ to $+1.02$, and $\Sigma_v - \Sigma_s$ varies from 24 to 40%). These data agree with the assumption that the hydrocarbon is

1:3-dimethyl-5-methylene- Δ^3 -cyclohexene, $\text{CH}_2 \begin{smallmatrix} \text{CMe} \\ \text{CHMe} \end{smallmatrix} \text{CH} \text{C}(\text{CH}_3)_2$

and belongs to the third system referred to above. On oxidation with permanganate, it furnishes a saturated neutral substance, $\text{C}_8\text{H}_{14}\text{O}$, m. p. 96—97°, but on treatment with ozone in acetic acid it yields γ -acetyl- β -methylbutyric acid (Knocvenagel and Brunswick, *Abstr.*, 1902, i, 640), identical with that obtained by the action of permanganate or ozone on 1:3-dimethyl- Δ^3 -cyclohexen-5-one, which is probably formed as an intermediate product in the oxidation of the hydrocarbon. γ -Acetyl- β -methylbutyric acid bas b. p. 140—142°/12 mm., D_4^{17} 1.0614, $n_D^{17.2}$ 1.44383, $n_D^{16.2}$ 1.44611, and yields a crystalline semicarbazone, m. p. 170—171°. The hydrocarbon on bromination and subsequent treatment with potassium hydroxide in alcohol yields mesitylene.

1:3-Dimethyl-5-ethylidene- Δ^3 -cyclohexene, b. p. 178°, D_4^{20} 0.833 to 0.837, n_D^{20} 1.476 to 1.483, n_D^{19} 1.480 to 1.487 (whence $\Sigma_s = +0.80$ to $+1.05$, $\Sigma_D = +0.84$ to $+1.10$, and $\Sigma_v - \Sigma_s = +27$ to 40%), probably identical with Klages' dihydroethylxylene (*Abstr.*, 1907, i, 597), is obtained by heating the corresponding tertiary alcohol alone or with oxalic acid.

1:3-Dimethyl-5-isopropylidene- Δ^3 -cyclohexene, similarly prepared, has b. p. 101°/36 mm. or 196°/760 mm., D_4^{20} 0.841 to 0.848, n_D^{20} 1.481 to 1.492, n_D^{19} 1.485 to 1.496 (whence $\Sigma_s = +0.70$ to $+1.20$, $\Sigma_D = +0.73$ to $+1.26$, and $\Sigma_v - \Sigma_s = 33$ to 51%). These hydrocarbons agree in general properties with the similar products containing semicyclic double linkings described by Wallach (*Abstr.*, 1907, i, 425), but possibly all of them contained isomerides having two endocyclic double linkings.

Pure hydrocarbons of this type probably have $\Sigma_e = +1.0$ to 1.2 , $\Sigma_D = +1.1$ to 1.3 , and $\Sigma_\gamma - \Sigma_a = 40$ to 50% . T. A. H.

Reducibility of Conjugated Double Linkings in Hydroaromatic Substances. KARL AUWERS and G. PETERS (*Ber.*, 1910, 43, 3111—3120).—An extension of the work described in the preceding abstract and this vol., i, 841. The results resemble those obtained by Klages (*Abstr.*, 1904, i, 45, 1001) in the case of styrene derivatives, and show that the reducibility of the hydroaromatic hydrocarbons depends on the number, nature, and distribution of the side-chains attached to the carbon atoms in the double linkings of the conjugated system. This influence has been illustrated already by the reduction of 3-chloroisoterpinolene to a mixture of menthenes (this vol., i, 122), by Semmler's reduction of chlorocarvenene to the corresponding hexadiene under similar conditions, and by the non-reducibility of hydrocarbons of this type, described by Rupe and Emmerich (*Abstr.*, 1908, i, 556).

5-Chloro-1:3-dimethyl- $\Delta^{3,5}$ -cyclohexadiene, already prepared by Klages and Knoevenagel (*Abstr.*, 1895, i, 654), has b. p. $68-70^\circ/17$ mm., $D_4^{25} 1.0065$, $n_D^{25} 1.50022$, $n_D^{20} 1.50459$ (whence $\Sigma_D = +0.69$), but the sample was probably not quite pure. On careful reduction with sodium in wet ether it yielded 1:3-dimethyl- $\Delta^{3,5}$ -cyclohexadiene, b. p. $128-129^\circ/760$ mm., $D_4^{25} 0.821$, $n_D^{25} 1.467$, $n_D^{20} 1.471$ (whence $\Sigma_e = +0.62$, $\Sigma_D = +0.68$, and $\Sigma_\gamma - \Sigma_a = 26\%$), which furnished a *dihydrochloride*, b. p. $93-97^\circ/16$ mm., and is possibly identical with the *dihydro-m-xylene* described by Harries and Antoni (*Abstr.*, 1903, i, 614), the difference in physical constants being perhaps due to impurity in both specimens. On further reduction in ether or, better, in alcohol, the chlorodimethylcyclohexadiene furnishes 1:3-dimethyl- Δ^1 -cyclohexene, b. p. $126-127^\circ/760$ mm., $D_4^{25} 0.806$, $n_D^{25} 1.447$, $n_D^{20} 1.450$ (whence $\Sigma_e = +0.26$, $\Sigma_D = +0.24$, and $\Sigma_\gamma - \Sigma_a = +9\%$) (compare Knoevenagel, *Abstr.*, 1897, i, 606), which yields a *mono-hydrochloride*. T. A. H.

Derivatives of 1:3-Dichloro-4-iodobenzene with a Multi-valent Iodine Atom. CONRAD WILLGERONT and MATTHIAS BOLLERT (*Ber.*, 1910, 43, 2641—2646).—2:4-Dichloroaniline is best prepared by the action of concentrated hydrochloric acid and potassium chlorate on acetanilide and subsequent hydrolysis of the acetyl derivative by boiling with hydrochloric acid. A small amount of *s*-trichloroaniline is formed at the same time, but this is readily removed, as it is insoluble in hydrochloric acid. The dichloroaniline can be transformed into the corresponding 1:3-dichloro-4-iodobenzene, $C_6H_3Cl_2I$, by the Sandmeyer reaction. The iodo-derivative has b. p. 257° (corr.), and yields a *dichloride*, $C_6H_3Cl_2 \cdot ICl_2$, in the form of pale yellow needles, which decompose at 107° . 1:3-Dichloro-4-iodosobenzene, $C_6H_3Cl_2 \cdot IO$, is a yellow-coloured powder with the characteristic iodoso-odour, and decomposes at about 196° . It does not yield stable salts. The *chromate* forms a red powder. *Di-m-dichlorophenyl-iodonium hydroxide*, $(C_6H_3Cl_2)_2I \cdot OH$, yields a faintly alkaline aqueous solution; the *iodide*, $(C_6H_3Cl_2)_2I \cdot I$, forms a yellow, crystalline precipitate, which decomposes at 135° ; the *bromide* decomposes at 159° ; the *chloride*, $(C_6H_3Cl_2)_2I \cdot Cl$,

is more readily soluble, and decomposes at 185° ; the *platinichloride*, $C_{24}H_{12}Cl_{14}I_2Pt$, forms red needles, decomposing at 166° ; the *mercurichloride*, $C_{12}H_6Cl_2IHg$, crystallises from alcohol in needles, m. p. 164° (decomp.), and the *dichromate*, $C_{24}H_{12}O_7Cl_3I_2Cr_2$, forms an orange-coloured precipitate, which is very unstable and explodes at 151° .

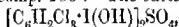
o-Tolyl-1:3-dichlorophenyliodonium iodide, $C_6H_4Me \cdot I(C_6H_3Cl_2)_2$, prepared by Meyer and Hartmann's method (Abstr., 1894, i, 242) by shaking equivalent quantities of *o*-iodotoluene and 1:3-dichloro-4-iodobenzene with freshly precipitated silver oxide and water and reducing with sulphur dioxide, is yellow, and has m. p. 127° . The *hydroxide* is soluble in water, yielding a faintly alkaline solution; the *chloride*, $C_{13}H_{10}Cl_3I$, is colourless, and has m. p. 203° ; the *bromide*, $C_{13}H_{10}Cl_2BrI$, crystallises from ether in plates, sinters at 170° , and decomposes at 185° ; the *nitrate*, $C_{13}H_{10}O_3NCl_3I$, has m. p. 183° (decomp.); the *dichromate*, $C_{26}H_{20}O_7Cl_3I_2Cr_2$, is yellow, and decomposes at 141° ; the *mercurichloride*, $C_{13}H_{10}Cl_2IHg$, forms colourless needles, m. p. 163° .

Phenyl-1:3-dichlorophenyliodonium iodide, $C_6H_5Cl_2 \cdot IPh \cdot I$, is yellow, but turns red on exposure to the air, and has m. p. 133° ; the *chloride*, $C_{12}H_9Cl_3I$, crystallises in colourless needles, m. p. 203° ; the *bromide* crystallises from alcohol in plates, m. p. 196° ; the *platinichloride*, $C_{24}H_{16}Cl_{10}I_2Pt$, forms yellow needles, m. p. 156° (decomp.), and the *dichromate*, $C_{22}H_{16}O_7Cl_3I_2Cr_2$, has m. p. 146° (decomp.).

1:3-Dichlorophenyl-1:3-dichloro-4-iodophenyliodonium chloride, $C_6H_3Cl_2 \cdot I(C_6H_3Cl_2)_2Cl$, crystallises from alcohol, and has m. p. 160° ; the *bromide* crystallises in colourless needles, m. p. $131-132^{\circ}$; the *iodide*, $C_{12}H_9Cl_3I_2$, has m. p. 103° ; the *dichromate*, $C_{22}H_{16}O_7Cl_3I_2Cr_2$, decomposes at 173° , and the *platinichloride*, $C_{24}H_{16}Cl_{10}I_2Pt$, forms a sparingly soluble, orange-coloured precipitate, m. p. 156° , after softening at 145° .
J. J. S.

Limits of Activity of Chloromonoiodobenzenes with Regard to the Formation of Compounds with Multivalent Iodine. CONRAD WILLGERODT and KARL WILCKE (*Ber.*, 1910, 43, 2746-2756). —*s*-Trichlorophenyl iododichloride, $C_6H_3Cl_3 \cdot ICl_2$, crystallises in large, compact, sulphur-coloured leaflets, decomp. 100° .

s-Trichloroiodosobenzene is a slightly yellow, amorphous substance, which softens at 91° , decomp. 106° . The *basic sulphate*,



prepared by pouring 10% sulphuric acid on the iodoso-compound, is a colourless, crystalline powder, decomp. 168° . The *basic nitrate* is a bright yellow, crystalline mass, decomp. 143.4° , with evolution of red fumes. The *acetate* is obtained in colourless prisms grouped in rosettes, m. p. 166.8° .

s-Trichloroiodoxybenzene could not be obtained from the iodoso-compound.

Phenyl-s-trichlorophenyliodonium chloride, $C_6H_5Cl_2 \cdot IPhCl$, is a yellow powder, m. p. $118-119^{\circ}$. The corresponding *iodide* begins to fuse at 90° , is melted clear at $140-150^{\circ}$, decomp. above 200° .

as *Trichlorophenyl iododichloride* crystallises in small, sulphur coloured needles, decomp. 90° .

as *Trichloriodosobenzene* softens at 168° , decomp. 184° .

as *Trichloriodoxybenzene*, $C_6H_2Cl_3 \cdot IO_2$, prepared by oxidation of the iodide chloride with sodium hypochlorite, forms needles, decomp. 240° without explosion.

as *Tetrachloroaniline* has m. p. 89° . as *Tetrachloriodobenzene* does not form an iododichloride, and parts with iodine when chlorinated. *Pentachloroaniline* has m. p. 232° . On diazotisation and addition of potassium iodide, *pentachloriodobenzene* is obtained in colourless crystals, m. p. 208.5° ; it does not give an iododichloride.

It would seem that no iodoxy-compound is formed when iodine is situated between two halogen atoms; apparently these exercise a neutralising influence on the valency of the iodine atom, and prevent the attachment of the second oxygen atom.

E. F. A.

Action of Nitric Acid on Saturated Hydrocarbons. IV.
S. S. NAMEKIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 581—585. Compare Abstr., 1909, i, 372).—When saturated hydrocarbons are nitrated with nitric acid, it is found that with the diminution of the relative quantity of the latter, the nitration products increase, whilst the oxidation processes decrease. Now, aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$, melts at 73° , and decomposes completely into aluminium hydroxide and nitric acid at 140° , and between these two temperatures there is a certain equilibrium between the salt and its decomposition products. If, therefore, this salt is used for nitration, within these temperature limits the nitric acid will be used up as formed, and the equilibrium will thus be constantly disturbed. The acid will thus always be present in a relatively small quantity; the yield of nitration products should, therefore, be better than if an equivalent quantity of free nitric acid were employed. Experiments with *cyclohexane* at $115-120^{\circ}$ completely confirmed these considerations, a yield of 56.7% of mononitro-product being obtained; free nitric acid has never given such a high yield. *cycloHexanone*, possibly its nitro-derivative, $C_6H_{11}O_2N$, and *dinitrodicyclohexane*, $C_{12}H_{20}O_2N_2$, m. p. $216.5-217^{\circ}$ (corr.) were formed as by-products. The latter, crystallising in small needles, was also obtained synthetically.

Z. K.

cycloHexyl-ψ-nitrole. S. S. NAMEKIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 585—586).—When a few pieces of ice and then dilute sulphuric acid are added to a mixture of an alkaline solution of nitro-*cyclohexane* and sodium nitrite, a blue oil at once separates, and collects at the bottom of the vessel. After some time, the oil is gradually converted into colourless crystals, which rise to the top of the liquid. These two substances are regarded as two modifications of the *ψ-nitrole*, the blue liquid being unimolecular, the solid, bimolecular.

Solid *cyclohexyl-ψ-nitrole*, $C_6H_{11}O_2N_2$, m. p. $70-71^{\circ}$ (decomp.), gives a blue solution in chloroform, and is oxidised by chromic acid in acetic acid solution, forming 1:1-*dinitrocyclohexane*, b. p. $142-143^{\circ}/35$ mm., D_4^{20} 1.2452, n_D^{20} 1.4732, a heavy, yellow oil with a fairly pleasant odour.

Z. K.

Action of Nitric Acid on Methylcyclohexane. S. S. NAMETSKIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 691—701).—When methylcyclohexane is nitrated with nitric acid (D 1.2) or aluminium nitrate in a sealed tube, the chief product is the 1-nitro-derivative, the 3- and 4-nitro-derivatives also being obtained, more of the former when nitric acid is employed, and more of the latter with aluminium nitrate.

1-Nitro-1-methylcyclohexane, $C_7H_{13}O_2N$, b. p. 109—110°/40 mm., D_4^{20} 1.0547, D_4^{25} 1.0384, n_D^{20} 1.4580, is a colourless liquid with a pleasant odour; when heated with nitric acid, it is partly oxidised to succinic and oxalic acids, and with tin and hydrochloric acid it yields 1-amino-1-methylcyclohexane.

3-Nitro-1-methylcyclohexane, mixed with a very small quantity of the 1-nitro-derivative, has b. p. 119—120°/40 mm., D_4^{20} 1.0547, D_4^{25} 1.0382, n_D^{20} 1.4618, yields on reduction 3-amino-1-methylcyclohexane, b. p. 152—153°/752 mm., D_4^{20} 0.8562, n_D^{20} 1.4558, which is optically inactive, and gives a benzoyl derivative, m. p. 95—97°. As a by-product in the formation of the amine, 1-methylcyclohexan-2-one, $C_7H_{12}O$, is obtained; the latter compound is also formed by the oxidation of an alkaline solution of the nitro-compound with potassium permanganate, or by the action of sulphuric acid on the potassium nitro-compound. It has b. p. 163—169° (corr.), D_4^{20} 0.9179, n_D^{20} 1.4453, and yields two semicarbazones, m. p. 172—180° and 167—169°. When oxidised with permanganate, the nitro-compound yields α - and β -methyladipic acids.

Nitrocyclohexane, b. p. 123—124°/40 mm., D_4^{20} 1.0459, n_D^{20} 1.4684, seems identical with the substance obtained by Zelinsky (*Abstr.*, 1908, i, 864). When oxidised, it yields adipic acid. Besides nitro-compounds, nitric acid, when acting on methylcyclohexane, yields a number of oxidation products, namely, adipic, succinic, oxalic, glutaric, and pyrotartaric acids. The nature of the oxidation processes is discussed.

The nitro-compound from naphtha methylcyclohexane could not be obtained pure. The impure product has b. p. 109—110°/40 mm., D_4^{20} 1.0234, D_4^{25} 1.0430, n_D^{20} 1.4553. With tin and hydrochloric acid it gave an amine, b. p. 143—145°/755 mm., D_4^{20} 0.8632, D_4^{25} 0.8493, n_D^{20} 1.4509, the benzoyl derivative, $C_7H_{13} \cdot NH \cdot COPh$, of which has m. p. 99—100°. Z. K.

Reduction of Nitro-derivatives by Spongy Copper. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1910, [iv], 7, 952—956).—Bougault has observed (*Abstr.*, 1909, ii, 310; compare Bach, this vol., ii, 31) that sodium hypophosphite added to copper sulphate solution furnishes a precipitate of spongy copper, which, in presence of sodium hypophosphite, decomposes water, liberating hydrogen. This process has been applied to the reduction of nitro-derivatives dissolved in alcohol, and gives good yields, complete in some cases, of the corresponding amines. The presence of halogen atoms or hydroxy-groups in the nitro-derivatives does not impede the reaction, and the halogen or hydroxy-group remains unattacked in the aromatic nucleus. The reaction is likely to be useful in the manu-

facture of aminophenols. Reduction is not effected when hydrogen under pressure is applied to a suspension of spongy copper in a solution of a reducible substance.

The substance to be reduced is dissolved in alcohol and placed in a flask with spongy copper. The flask is provided with a stopper carrying a reflux apparatus, and a bromine tube holding a supply of sodium hypophosphite solution, which is added from time to time as the action slackens. The nitro-derivatives tried include the following: nitroethane, *o*- and *p*-nitrotoluene, *o*-chloronitrobenzene, *p*-bromonitrobenzene, nitronaphthalene, *o*-nitrophenol, and 2:3-dinitrophenol.

T. A. H.

Spontaneous Decomposition of Phenylnitromethane. OTTO DIMROTH (*Ber.*, 1910, 43, 2767—2768).—Crystals of dibenzhydroxamic acid, m. p. 161°, were obtained in quantity from phenylnitromethane preparations which had been kept for a long time.

E. F. A.

Some New Derivatives of Diphenylmethane. LUIGI MASCARELLI, B. TOSCHI, and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 338—342. Compare Mascarelli, this vol., i, 725).—4:4'-Dichloro-2:2'-dinitrodiphenylmethane, obtained by means of the Sandmeyer reaction from the corresponding diamino derivative, forms slightly yellow, rhombic tablets, m. p. 121—122°. On reduction with tin and hydrochloric acid in alcoholic solution it yields 4:4'-dichloro-2:2'-diaminodiphenylmethane, which crystallises in colourless needles, m. p. 130—131°. When diazotised and treated with potassium iodide, it is converted into 4:4'-dichloro-2:2'-diiododiphenylmethane, which forms colourless crystals, m. p. 77—78°.

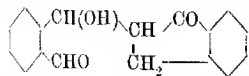
2:2'-Di-iodo 4:4'-tetramethyldiaminodiphenylmethane,



can be obtained, but only in small amount, by diazotising the corresponding amino-compound and treating it with potassium iodide. It forms colourless scales, m. p. 123°.

R. V. S.

Derivatives of isoNaphthfluoren (*o*-Phenylene- $\beta\beta$ -naphthyl-enemethane). JOHANNES THIELE and ALEXIS WANSCHIEDT (*Annalen*, 1910, 376, 269—279).—A modification of Kipping's method of preparing α -hydrindone (*Trans.*, 1891, 65, 485) from β -phenylpropionyl chloride (which is best prepared by warming β -phenylpropionic acid with thionyl chloride) is described, whereby the ketone is obtained in 95% yield. It reacts with *o*-phthalaldehyde and 10% sodium hydroxide in aqueous alcohol to form an additive compound, $\text{C}_{17}\text{H}_{11}\text{O}_3$, m. p. 185° (decomp.), which receives the annexed constitution (2 *o*-hydroxy-*o*-aldehydobenzyl-1-hydrindone) because it



reduces ammoniacal silver nitrate and is converted into isonaphthfluorenone (*o*-phenylene- $\beta\beta$ -naphthylene ketone) (*Abstr.*, 1909, i, 929)

by boiling methyl-alcoholic potassium hydroxide. A better method is described for the preparation of isonaphthfluorenone. It forms an *urine*, m. p. 231°, and by reduction with sodium amalgam or with zinc and potassium hydroxide, is converted into isonaphthfluorenol,

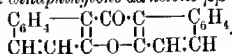
$\text{OH}\cdot\text{CH}<\text{C}_6\text{H}_4$, m. p. 185°. This alcohol forms an ether, $\text{O}(\text{C}_{17}\text{H}_{11})_2$ (?), m. p. about 300°, an acetate, m. p. 97°, and in glacial acetic acid is converted by hydrogen chloride into the chloride, $\text{C}_{17}\text{H}_{11}\text{Cl}$, m. p. 150°, and by hydrogen bromide in glacial acetic acid into the bromide, $\text{C}_{17}\text{H}_{11}\text{Br}$, m. p. 162° (decomp.), which is reduced to isonaphthylfluorene, $\text{C}_{17}\text{H}_{12}$, m. p. 208°, by zinc and acetic and hydrochloric acids. Diisonaphthylfluorenyl, C_{10}H_6
 C_6H_4 $\text{CH}\cdot\text{CH}<\text{C}_6\text{H}_4$, m. p. 260—270° (decomp.), is obtained by heating isonaphthylfluorenyl bromide and sodium iodide in acetone. Bisphenylene-bis- $\beta\beta$ -naphthylene-ethylene, C_{10}H_6
 C_6H_4 $\text{C}\equiv\text{C}<\text{C}_6\text{H}_4$, m. p. 232°, obtained by the interaction 5*N*-methyl-alcoholic potassium hydroxide and isonaphthylfluorenyl bromide in an excess of acetone, crystallises in dark red leaflets; it can also be prepared by heating isonaphthylfluorene or diisonaphthylfluorenyl with lead oxide at 300°, and is reduced to the latter by sodium amalgam and boiling amyl alcohol. C. S.

Dinaphthylmethane and Naphthylfluorene. JULIUS SCHMIDT and MAX HUBER (*Ber.*, 1910, 43, 2821—2837).—The three dinaphthylmethanes which are theoretically possible are all known, but the constitution of only one has been determined with certainty, namely, di- β -naphthylmethane, m. p. 92°, prepared by reducing di- β -naphthyl ketone (Richter, *Abstr.*, 1881, 281). It is now shown that the hydrocarbon obtained by Grabowski (*Abstr.*, 1875, 455) by condensing naphthalene with methylal in the presence of sulphuric acid is di- α -naphthylmethane, since it can be prepared from di- α -naphthyl carbinol by converting the latter into di- α -naphthylacetic acid, and distilling the acid when carbon dioxide is eliminated. The hydrocarbon described by Claus and Ruppel (*Abstr.*, 1890, 510) must therefore be $\alpha\beta$ -dinaphthylmethane.

The constitutions of the isomeric dinaphthaxanthenes have also been established. The three isomerides formed from β -naphthol must have the O-bridge in the β -position in both naphthalene rings. The compound with m. p. 149° (Claus and Ruppel, *loc. cit.*) yields $\alpha\beta$ -dinaphthylmethane when reduced, and must therefore be di-

naphthylene- $\alpha\beta$ -ketone- $\beta\beta$ -oxide, C_6H_4 — $\text{C}\equiv\text{CO}\cdot\text{C}\equiv\text{CH}$
 $\text{CH}\cdot\text{CH}\cdot\text{C}\equiv\text{O}\cdot\text{C}\equiv\text{CH}$ C_6H_4 . Bender's

β -dinaphthaxanthone, m. p. 194° (*Abstr.*, 1887, 37), must have the carbonyl group in the α -position with respect to one naphthalene ring (Kostanecki, *Abstr.*, 1892, 1098), and since it is not identical with Claus and Ruppel's xanthone, the carbonyl group must be in the α -position with respect to the second naphthalene ring, and the compound is therefore *dinaphthylene- $\alpha\alpha$ -ketone- $\beta\beta$ -oxide*,



γ -Dinaphthaxanthone, m. p. 241° (Kostanecki, *loc. cit.*), must be

dinaphthylene- $\beta\beta$ -ketone- $\beta\beta$ -oxide, C_6H_4 $\text{CH}\cdot\text{C}\equiv\text{CO}\cdot\text{C}\equiv\text{CH}$ C_6H_4 .

Di- α -naphthylacetic acid, $(C_{10}H_7)_2CH \cdot CO_2H$, obtained by converting di- α -naphthylcarbinol (Schmidlin and Massini, Abstr., 1909, i, 561) into the carbonyl chloride, and then condensing this with magnesium and carbon dioxide, has m. p. 223° , and when heated at 250 — 260° and then at 300° yields di- α -naphthylmethane, m. p. 105° (corr.). Grabowski's hydrocarbon has the same melting point, and in its preparation according to Grabowski's method appreciable amounts of a compound, $C_{40}H_{32}O$, are obtained.

β -Iodonaphthalene is prepared readily by a modification of Jacobson's method (Abstr., 1881, 736), and the magnesium β -naphthyl iodide reacts with a dry ethereal solution of ethyl formate, yielding a product which is decomposed by dilute acid, giving di- β -naphthylcarbinol, β -dinaphthylfluorene, naphthalene, and another product.

$\beta\beta$ -*Dinaphthylfluorene*, $\begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > CH_2$ is somewhat sparingly soluble in cold ether, but is more soluble than the carbinol in hot light petroleum. It crystallises in large, colourless, macroous plates, m. p. 190.5° (corr.), and its solutions do not fluoresce. It is isomeric with Bamberger and Chattaway's picylenemethane (Abstr., 1895, i, 233), and when oxidised with an acetic acid solution of chromic anhydride yields $\beta\beta$ -*dinaphthylfluorenone*, $\begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > CO$, which crystallises from ether in large, orange-coloured needles, m. p. 163 — 165° (corr.). The ketone dissolves in concentrated sulphuric acid, yielding deep blue-coloured solutions, which turn brown when kept. The isomeric *aa-dinaphthylfluorenone*, prepared by oxidising *aa*-dinaphthylfluorene (Schmidlin and Massini, *loc. cit.*), crystallises in minute, deep red-coloured needles, m. p. 255° , and dissolves in concentrated sulphuric acid to red solutions.

Di- β -naphthylcarbinol, $CH(C_{10}H_7)_2 \cdot OH$, crystallises from light petroleum (b. p. 110 — 150°) in nodular masses, m. p. 91° (corr.), containing petroleum of crystallisation. The carbinol also forms a definite compound with hexane, $C_{21}H_{16}O, 2C_6H_{14}$; this has m. p. 116.5° (corr.), and the hexane is removed when the crystals are heated at 150° under reduced pressure. The carbinol has not been obtained in a crystalline form free from hydrocarbon of crystallisation.

Di- β -naphthylchloromethane, $CH(C_{10}H_7)_2Cl$, obtained by the action of hydrogen chloride on a warm benzene solution of the carbinol, crystallises in colourless prisms, m. p. 167° (corr.). Its solution in concentrated sulphuric acid is colourless, but gradually assumes a violet coloration, due to the formation of the carbinol. It reacts with water or concentrated sulphuric acid less readily than the isomeric *aa*-compound does. *Di- β -naphthylacetic acid*, $CH(C_{10}H_7)_2 \cdot CO_2H$, crystallises from glacial acetic acid in felted needles, m. p. 182 — 183° (corr.), and yields a sparingly soluble sodium salt. In the preparation of the acid an appreciable amount of *tetra- β -naphthylethane*,

$CH(C_{10}H_7)_2 \cdot CH(C_{10}H_7)_2$, is formed. It crystallises from benzene in small prisms, m. p. 273.5° (corr.).

Tetra- α -naphthylethane (Schmidlin and Massini, *loc. cit.*), when

oxidised with chromic anhydride, yields an oxide, $C_{12}H_{28}O$, in the form of orange-red crystals, m. p. 257° .

Attempts to prepare di- α -naphthylketen-quinoline were unsuccessful.

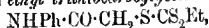
Attempts to prepare tri- β -naphthylcarbinol by the action of β -naphthoyl chloride on magnesium β -naphthyl bromide gave an appreciable amount of an impure hydrocarbon, probably tri- β -naphthylmethane, m. p. 178° .

J. J. S.

Some Amide Derivatives of Thiocarboglycollic Acid. From HOLMBERG and B. PSILANDERHJELM (*J. pr. Chem.*, 1910, [ii], 82, 440—459). Compare this vol., i, 361).—In the production of rhodanins from dithiocarbamates and chloroacetamide (Miolati, Abstr., 1893, i, 403), the authors find that the amino-group of the acetic acid derivative is always eliminated by the ring closure, the thiocarbonyl group exhibiting remarkable stability. This conclusion is drawn from experiments on the behaviour of chloroacetamide and of chloroacetanilide on *N*-substituted dithiocarbamates; thus, chloroacetamide reacts easily with aqueous potassium phenyldithiocarbamate (prepared from aqueous potassium hydroxide, aniline, and carbon disulphide, a little *s*-diphenylthiocarbamide, which is formed, being removed by filtration) to form *N*-phenylrhodanin. Chloroacetanilide and aqueous ammonium dithiocarbamate give, according to the conditions of the experiment, either thiocarbonylthioglycollanilide (which is converted into rhodanine by hot dilute sulphuric acid) or a mixture of trithiocarbodiglycollanilide and thiodyglycollanilide; alcoholic chloroacetanilide and aqueous ammonium dithiocarbamate yield only thiodyglycollanilide. Chloroacetamide and aqueous potassium *o*-tolylidithiocarbamate yield *N*-*o*-tolylrhodanine.

Phenylmethylthiocarbonylthioglycollic acid, $CO_2H \cdot CH_2 \cdot S \cdot CS \cdot NPhMe$, m. p. $197-198^{\circ}$ (decomp.), is obtained by heating aqueous trithiocarbodiglycollic acid and methylaniline, or, much better, by treating aqueous potassium phenylmethyldithiocarbamate with aqueous sodium chloroacetate and acidifying after one day; it forms an ethyl ester, m. p. 77° . The amide, $NPhMe \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH_2$, m. p. $141-141.5^{\circ}$, obtained from chloroacetamide and aqueous potassium phenylmethyldithiocarbamate, is converted into the free acid by hot dilute sulphuric acid, and into the ethyl ester by alcoholic sulphuric acid. The anilide, $NPhMe \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NHPh$, m. p. $139-139.5^{\circ}$, obtained from chloroacetanilide and potassium phenylmethyldithiocarbamate, is unchanged by hot dilute sulphuric acid, and is converted into the ethyl ester by alcoholic sulphuric acid.

Ethyl xanthoacetanilide, $OEt \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NHPh$, m. p. $91.5-92^{\circ}$, obtained from chloroacetanilide and potassium xanthate in aqueous alcoholic solution, and **ethyl trithiocarboglycollanilide**,



m. p. 98° , obtained from chloroacetanilide and potassium ethyl trithiocarbonate, do not yield *N*-phenylrhodanine by elimination of alcohol and ethyl mercaptan respectively.

C. S.

Isomerism in Compounds with Two Similar Asymmetric Nitrogen Atoms. EDGAR WEDEKIND and OTTO WEDEKIND (*Ber.*, 1910, 43, 2707—2719).—Trimethylene-bis(phenylmethylethylammonium

iodide), $\text{CH}_3(\text{CH}_2\cdot\text{NMeEtPhI})_2$, has been prepared in two ways: by the action of 2 mols. of methyl iodide on trimethylene-bis-ethylaniline, and by the addition of ethyl sulphate to trimethylene-bis-methylaniline, and interaction of the product with potassium iodide. In both cases the product obtained was a mixture of two isomeric iodides, a small quantity of a monomethiodide being also formed by the first method. The difference between the two iodides persists in their derivatives: those derived from the less fusible iodide are distinguished as *meso*-, those from the more fusible iodide as *para*-compounds. The *meso-iodide* has decomp. 222° , and crystallises in transparent prisms; the *para-iodide* forms opaque, prismatic aggregates (decomp. 177°). The *meso-platinichloride* forms monoclinic plates (decomp. 222°); the *isomeride* crystallises in monoclinic prisms, also m. p. 222° . The *meso-aurichloride* has decomp. 215° ; the *para*-compound, decomp. 205 – 206° . The *meso-picrate* has m. p. 129° , forming indefinite crystals; the transparent prisms of the *para-picrate* show m. p. 165° . The *meso-d-camphorsulphonate* forms prismatic needles, m. p. 118 – 120° ; the *para-isomeride* is very similar, m. p. 116 – 118° . The *meso-d-bromocamphorsulphonate* is crystalline, m. p. 163° ; the *isomeride* is amorphous.

It has not been possible to transform salts of one series into the other.

Fractional crystallisation of the camphorsulphonates and bromocamphorsulphonates did not resolve either base into optically active forms.

Trimethylene-bis-ethylaniline (compare Fröhlich, Abstr., 1907, i, 346) has b. p. 240 – $242^\circ/20$ mm.

Trimethylene-bis(*phenyldimethylammonium iodide*) crystallises in needles (decomp. 216°). E. F. A.

Electrolytic Reduction of Aromatic Sulphonyl Chlorides.

FRITZ FICHTER and WALTER TAMM (*Ber.*, 1910, 43, 3032–3038. Compare this vol., i, 20).—Suspensions of various aromatic sulphonyl chlorides in alcoholic sulphuric acid were reduced at a rotating lead cathode in a divided cell, the temperature being kept down by using a coiled lead tube, through which cold water flowed, as the anode. The most favourable current density varies from 0.04–0.07 ampere per sq. cm.; a further increase in the current density simply leads to the evolution of hydrogen. A copper cathode gives practically the same yield as one of lead, but with cathodes of silver, iron, zinc, nickel, or platinum the yield decreases in the order mentioned. Usually about one and a-half times the theoretical current was passed, the resulting product being a mixture of the disulphide, mercaptan, and sulphinic acid. To isolate these the reaction mixture was made alkaline with ammonia and the mercaptan oxidised by a current of air. After collecting the disulphide, sodium nitrite was added to the filtrate, and, after acidification with dilute sulphuric acid, a precipitate of the diarylsulphonylhydroxylamine derived from the sulphoic acid was obtained. These compounds are generally readily soluble in alkalis or alcohol, but sparingly so in benzene or ether.

α -Naphthalenesulphonyl chloride gave a yield of 81.3% of α -naphthyl disulphide and 13.6% of α -naphthalenesulphinic acid. The *di- α -naphthyl-*

sulphonylhydroxylamine, $(C_{10}H_7SO_2)_2N \cdot OH$, forms crystals, which have m. p. $120-130^\circ$ (decomp.). The solutions decompose on warming into tri- α -naphthylsulphonamide. β -Naphthalenesulphonyl chloride gave an 80% yield of the β -naphthyl disulphide and 12.6% yield of β -naphthalenesulphinic acid. *Di- β -naphthylsulphonylhydroxylamine* separated as almost colourless crystals from dilute alcohol; it decomposes at 134° . From benzene-1:3-disulphonyl chloride, dithioresorcin was isolated by extracting the weakly acid solution with ether; yield 20—25%. The yield of benzene-1:3-disulphinic acid was 50%. Molecular-weight determinations in acetone of the corresponding disulphonylhydroxylamine showed it to be *bis-m-phenylenedisulphonylhydroxylamine*, $C_6H_4 \begin{smallmatrix} SO_2 \cdot N(OH) \cdot SO_2 \\ SO_2 \cdot N(OH) \cdot SO_2 \end{smallmatrix} C_6H_4$; colourless crystals, de. composing at 212° .

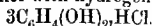
p-Anisolesulphonyl chloride gave a 25.7—37% yield of *p*-methoxyphenyl disulphide. *Di-p-methoxybenzenesulphonylhydroxylamine* forms white needles, m. p. 120° (decomp.). *m*-Nitrobenzenesulphonyl chloride gave a 65—70% yield of *m*-aminophenyl disulphide sulphate.

The reaction mixture resulting from the interaction of sodium dimethylanilinesulphonate and phosphorus pentachloride was shown to contain the sulphonyl chloride by the preparation from it of *p*-dimethylanilinesulphonamide, $NMe_2 \cdot C_6H_4 \cdot SO_2 \cdot NHPh$; colourless crystals from alcohol, m. p. 176° . The crude reaction mixture containing the sulphonyl chloride gave *dithiodimethylaniline*, $S_2(C_6H_4 \cdot NMe_2)_2$, on electrolytic reduction; m. p. 118° . The yield is very small because of the instability of the sulphonyl chloride. T. S. P.

Theory of Organic Reactions. Molecular Compounds as Preliminary Products in Cases of Condensation. I. JULIUS SCHMIDLIN and RUDOLF LANG (*Ber.*, 1910, 43, 2806—2820. Compare Uroczynski and Gaye, this vol., ii, 699).—The authors accept Fittig's view that chemical reactions are preceded by the formation of more or less unstable additive compounds (compare Michael, *Abstr.*, 1888, 1055; 1900, i, 321; 1904, ii, 64), and attention is drawn to the fact that in the case of triphenylmethyl derivatives and nitrosodimethylaniline chemical reactivity is accompanied by capacity for formation of additive compounds.

The examples investigated have been those of condensations which take place readily in the presence of a condensing reagent without the application of heat. In such cases the question is not complicated to any appreciable extent by the formation of additive compounds between the reacting substances and the condensing agent. The following pairs of substances have been examined: phenol and acetone, resorcinol and acetone, quinol and acetone, catechol and acetone, pyrogallol and acetone, and phenol and cyclohexanone. In those cases in which condensation takes place with great readiness, it is found that additive compounds are formed, and that the relative amounts of the components in the additive compound are the same as the relative proportions in which they react to form the condensation product. Catechol and acetone, and also quinol and acetone, condense but slowly in the presence of concentrated hydrochloric acid and the additive compounds,

and condensation products bear no simple relationship to one another. In the latter case, the question is complicated by the formation of a definite compound of quinol with hydrogen chloride,



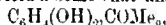
Similarly, the additive compounds and condensation products of pyrogallol and acetone, and of phenol and cyclohexanone, do not correspond.

In some cases the additive compounds have been actually isolated, and in all cases have been detected by melting-point curves.

Phenol and acetone yield the compound, $2Ph \cdot OH \cdot COMe_2$, in the form of long needles, m. p. 15° , and the condensation product, di- β -p-hydroxyphenylpropane, $CMe_2(C_6H_4 \cdot OH)_2$ (compare Dianin, Abstr., 1893, i, 214; Zincke and Grütters, *ibid.*, 1906, i, 172), which is formed most readily when cold concentrated sulphuric acid is used as condensing agent. When crystallised from benzene, it retains benzene on crystallisation, $3C_{12}H_{10}O_2 \cdot C_6H_6$, which it loses when heated at 80° under reduced pressure.

Resorcinol and acetone yield the compound, $C_6H_4(OH)_2 \cdot 2COMe_2$, m. p. 23° , which is comparatively stable. In determining melting points of mixtures of the two compounds, it is essential to avoid the entrance of traces of moisture, as such traces cause the mixtures to set to solid vitreous masses. The condensation product has not the composition stated by Causse (Abstr., 1892, 1312), but is to be represented as $C_{12}H_{11}O_6$. $C_6H_4(OH)_2 + 2CO(CH_3)_2 = C_{12}H_{14}O_2 + 2H_2O$, and has m. p. $230-240^\circ$.

Catechol and acetone yield a somewhat unstable compound,



m. p. -30° . The condensation product has the formula $C_{15}H_{14}O_4$, is formed in only small quantities, and decomposes at 270° . Quinol and acetone yield the compound, $C_6H_4(OH) \cdot COMe_2$, when sealed tubes are used (compare Habermann, Abstr., 1885, 53). Pyrogallol and acetone yield the compound, $C_6H_3(OH)_3 \cdot 3COMe_2$, m. p. -24° . The condensation product contains C = 68.4 and H = 6.3%.

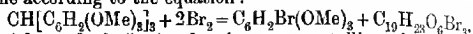
The compound of phenol and cyclohexanone, $PhOH \cdot C_6H_{10}O$, has m. p. -23° , and the condensation product, 1:1-di-p-hydroxyphenylcyclohexane, $C_6H_{10}(C_6H_4 \cdot OH)_2$, obtained by using concentrated sulphuric acid, crystallises in colourless, rhombic plates containing alcohol, m. p. 186° (corr.).

α -Naphthol and cyclohexanone react with concentrated sulphuric acid, yielding a product, $C_{26}H_{22}O$, m. p. 232° . This appears to be the anhydride of di- α -hydroxynaphthylcyclohexane, $C_6H_{10} \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} O$, and is insoluble in alkalis.

J. J. S.

An Easy Transformation of Asaryl Aldehyde into a Triphenylmethane Derivative. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1910, 43, 2676-2684).—A good yield of nonamethoxytriphenylmethane, $CH[C_6H_3(OMe)_3]_3$, is obtained when asaryl aldehyde is heated with 25% hydrochloric acid for three hours on a water-bath. It may be freed from a brown, amorphous by-product by treatment with very dilute alkali hydroxide, and separates from alcohol in

colourless crystals, m. p. 184.5°. Its solution in sulphuric acid has a brilliant blue colour, and the crystals tend to turn yellow when kept in a calcium chloride desiccator. Concentrated nitric acid reacts with a glacial acetic acid solution of the nonamethoxy-derivative, yielding 4-nitro-1:2:5-trimethoxybenzene (Abstr., 1907, i, 45). Bromine reacts with a cold benzene solution of the nonamethoxytriphenylmethane according to the equation:

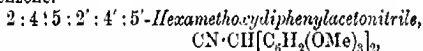


The 4-bromo-1:2:5-trimethoxybenzene crystallises from alcohol in colourless, monoclinic prisms [$\alpha:b=0.97506:1$; $\beta=50^\circ 56'$], m. p. 54.5°. The same compound can be prepared more readily by the action of bromine on asaronic acid, or by the bromination of hydroxy-quinol trimethyl ether. In the latter case, when an excess of bromine is used, dark blue, glistening crystals, $\text{C}_9\text{H}_{11}\text{O}_3\text{Br}_2$, are formed, but these are extremely unstable, and with water yield the bromotrimethoxybenzene. The second product, obtained by the action of bromine on the nonamethoxy-derivative, crystallises from benzene in slender prisms with a dark purple-blue colour, and is represented as a bromine additive compound of hexamethoxydiphenylmethane, namely,

$$\text{BrMeO}:\text{C} \begin{array}{c} \text{C}(\text{OMe})\text{:CH} \\ \text{CH}:\text{C}(\text{OMe}) \end{array} \text{C}:\text{CH}:\text{CBr} \begin{array}{c} \text{C}(\text{OMe})\text{:CH} \\ \text{CH}:\text{C}(\text{OMe}) \end{array} \text{C}:\text{OMeBr}.$$

This formula is supported by the fact that the compound reacts with water, yielding asarylaldehyde and bromotrimethoxybenzene, $\text{C}_{19}\text{H}_{23}\text{O}_6\text{Br}_3 + \text{H}_2\text{O} = \text{CHO}\cdot\text{C}_6\text{H}_3(\text{OMe})_3 + \text{C}_6\text{H}_2\text{Br}(\text{OMe})_3$.

Dibromotrimethoxybenzene, $\text{C}_6\text{H}_2\text{Br}_2(\text{OMe})_3$, prepared by the action of bromine on the monobromo-derivative, crystallises from benzene in long, colourless needles, m. p. 61°. 2:4:5:2':4':5'-Hexamethoxydiphenyl, $\text{C}_{12}\text{H}_4(\text{OMe})_6$, can be obtained from the bromotrimethoxybenzene and copper at 270°. It crystallises from alcohol, has m. p. 180°, and yields a greenish-blue, unstable, additive compound with benzene.

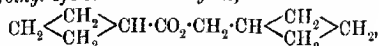


is formed by the action of silver cyanide on the bromine additive compound of hexamethoxydiphenylmethane: $\text{C}_{19}\text{H}_{23}\text{O}_6\text{Br}_3 + 3\text{AgCN} = \text{CN}\cdot\text{CH}[\text{C}_6\text{H}_2(\text{OMe})_3]_2 + 3\text{AgBr} + \text{C}_2\text{N}_2$, and crystallises from alcohol in slender needles, m. p. 155°.

Hydrogen chloride yields a deep blue additive compound with the nonamethoxytriphenylmethane, and when this is decomposed with water a colourless compound, m. p. 115–116°, is formed. J. J. S.

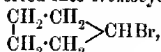
cycloButylcarbinol (ω -Hydroxymethylcyclobutane) and its Isomerisation Under the Influence of Acids into Pentane Derivatives. NICOLAUS J. DENJANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 837–855. Compare Abstr., 1903, i, 403; Perkin, *Trans.*, 1901, 70, 329).—The most convenient method of obtaining *cyclobutylcarbinol*, $\text{C}_4\text{H}_7\cdot\text{CH}_2\cdot\text{OH}$, is by the reduction of ethyl *cyclobutane*-carboxylate with metallic sodium in alcoholic solution. When pure, it has b. p. 140–142.5°/750 mm., D_{20}^{20} 0.9199, D_{20}^{25} 0.9129, n_D^{20} 1.4449. When oxidised with chromic anhydride and sulphuric acid, it forms an aldehyde, of which the sodium bisulphite compound and a semi-

carbazone, m. p. 115—120°, were prepared in an impure state, and *cyclobutylcarbinyl cyclobutanecarboxylate*,



b. p. 218—220°, D_{15}^{20} 0.9795, n_D^{19} 1.4546, n_D^{21} 1.4533.

When heated with hydrogen bromide in a sealed tube at 100°, *cyclobutylcarbinol* is converted into *bromocyclopentane*,



b. p. 137—139°, D_{15}^{20} 1.385, n_D^{19} 1.4875, which by means of zinc palladium and hydrobromic acid is reduced to *cyclopentane*,

b. p. 49—50°/750 mm., D_{15}^{20} 0.7525, D_{20}^{20} 0.7513, $n_D^{18.5}$ 1.4087, n_D^{20} 1.4072.

Iodocyclopentane, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CHI}$, prepared similarly, is a colourless liquid, which turns green or brown when kept, has b. p. 162—164°/750 mm. (decomp.), D_4^{20} 1.7154, D_4^{20} 1.6825, n_D^{20} 1.5374, and with silver nitrate yields a secondary and a primary nitro-compound, which, without being isolated, were converted into the ψ -nitrole, $\text{NO} \cdot \text{C}_5\text{H}_9 \cdot \text{NO}_2$, m. p. 96°.

With oxalic acid, *cyclobutylcarbinol* yields a hydrocarbon, b. p. 43.5—44°/755 mm., seemingly identical in physical properties with that obtained from ω -aminomethylcyclobutane, and probably consisting of a mixture of *cyclopentene*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH}$, and a *dicyclopentene*,

$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH} \end{array} \text{CH}_2$, or of the latter only.

The unsaturated hydrocarbon gives a *dibromide*, b. p. 192—195°, and with sulphuric acid an *alcohol*, b. p. 137—138°/753 mm., which with chromic anhydride and sulphuric acid yields *cyclopentanone*, b. p. 130—131.5°, from which the oxime, m. p. 57°, and dihenzyl derivative, m. p. 189°, were prepared. The constitution of the unsaturated hydrocarbon and the isomerisation of *cyclobutanes* into *cyclopentanes* is discussed.

Z. K.

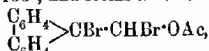
The Fluorene Series. A Correction. JULIUS SCHMIDT (*Ber.*, 1910, 43, 2778—2779).—The substance described as fluoreno ether by Schmidt and Stützel (this vol., i, 29) is, as Kliegl (this vol., i, 733) has in the meantime shown, a mixture of red diphenylene-ethylene and colourless diphenylenepheneanthrone.

E. F. A.

9-Formylfluorene or Diphenyleneacetaldehyde [Fluorene-9-aldehyde]. II. WILHELM WISLIZENUS and KARL RUSS (*Ber.*, 1910, 43, 2719—2734. Compare Abstr., 1909, i, 241).—In the pure state only the crystalline β -form and the polymeride of double molecular weight exist; the oily α -form is in reality the β -form hindered from crystallisation by impurities. Formylfluorene tends to polymerise when distilled; the vapour is unimolecular, but it polymerises during cooling. The enolic form is unstable, and no ferric chloride coloration is

produced. The enolic potassium compound gives no coloration, but a precipitate of ferric hydroxide.

The sodium bisulphite compound crystallises in colourless, flat needles, m. p. 151—152° (decomp.). The *O*-acetate crystallises in platelets, m. p. 132—133°, and forms a dibromide,



separating in colourless plates, m. p. 146—147° (decomp.). By the action of dry ammonia, a colourless compound, m. p. 148—149°, is formed, either iminomethylfluorene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{CH} \cdot \text{CH} \cdot \text{NH}$, or amino-

methylene-fluorene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{CH} \cdot \text{NH}_2$. When heated above the melting point, a yellow compound is formed, which crystallises from nitrobenzene in small, golden-yellow prisms, m. p. 316—317°.

This dissolves in alcoholic potassium hydroxide or sodium ethoxide with a bluish-red coloration, which slowly disappears on standing; this colour change is attributed to conversion into the desmotropic form.

Formylfluorenenonoethylanilide, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{CH} \cdot \text{NEtPh}$, prepared by interaction of the components, crystallises in slender, canary-yellow prisms, m. p. 95—96°. The corresponding piperidine derivative, prepared in alcoholic solution, crystallises in yellow plates.

Formylfluorene- α -oxime, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{CH} \cdot \text{CH} \cdot \text{N}(\text{OH})$, probably the *anti*-form, crystallises in colourless needles, m. p. 132—133°, colouring at 166°. The β -oxime, probably the *syn*-form, crystallises in similar needles, m. p. 166—167°.

9-Cyanofluorene [fluorene-9-carboxylonitrile], $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{CH} \cdot \text{CN}$, produced by the action of thionyl chloride on the oxime, forms long, lustrous, colourless needles, m. p. 151—152°. It dissolves in warm sodium hydroxide with a yellow colour and bluish-green fluorescence.

Formylfluorenebenzoylhydrazide separates in lustrous, light yellow needles, m. p. 233—234°. On evaporation of solutions of the phenylhydrazone, an oxidation product, m. p. 155—156°, is formed, probably an azo-compound. This reacts with bromine, forming a *p*-bromobenzene-azomethylene-fluorene dibromide, $\text{C}_{20}\text{H}_{13}\text{N}_2\text{Br}_2$, crystallising in dark red needles, m. p. 210—211°. It is more easily obtained from formylfluorene-*p*-bromophenylhydrazone, which crystallises in lustrous, yellow plates, m. p. 158—159° (decomp.), and yields *p*-bromobenzeneazomethylene-fluorene, $\text{C}_{13}\text{H}_8 \cdot \text{CH} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, on oxidation, crystallising in lustrous, deep red needles with a blue reflex, m. p. 187—188°, and dissolving in concentrated sulphuric acid with an intense violet coloration.

Formylfluorenehydrazone forms colourless, lustrous, silky needles, m. p. 158—160°; it readily undergoes oxidation to azomethylene-fluorene, $\text{C}_{13}\text{H}_8 \cdot \text{CH} \cdot \text{N} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_{13}\text{H}_8$, crystallising in very dark red, lustrous prisms, with a blue reflex, m. p. 290° (about).

Formylfluoreneacyanohydrin forms colourless, slender, silky needles,

m. p. 142—143°. When heated with concentrated hydrochloric acid in sealed tubes at 125°, *fluorene-9-glycollic acid*, $C_{13}H_9 \cdot CH(OH) \cdot CO_2H$, is formed in colourless plates, m. p. 194—195°. When boiled with potassium ethoxide, *cyanomethylenefluorene*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C:CH:CN$, is

obtained as a yellow, crystalline substance, m. p. 109—110°. It is remarkably stable towards hydrolysing agents.

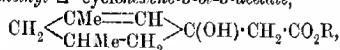
By the action of bromine on formylfluorene an oil is produced. When dissolved in alcohol, the *acetal*, $C_{15}H_{19}O_2Br$, crystallises in colourless needles, m. p. 119—120°.

Di-biphenylenesuccinaldehyde, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C(CHO) \cdot C(CHO) < \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}$, is obtained on oxidising formylfluorene with ferric chloride in acetic acid solution; it crystallises in colourless, lustrous prisms, m. p. 215—216°. Potassium ethoxide converts it into potassium formate and diphenylene-ethane, E. F. A.

Formation of an Ethylene Oxide from the Quaternary Base of Phenylmethylhydroxyethylamine. PAUL RABE and JULIUS HALLENSLEEN (*Ber.*, 1910, 43, 2622—2623. Compare this vol. i, 317).—It is shown that α -phenylpropylene $\alpha\beta$ -oxide is formed when the aqueous solution of Emde and Runne's (this vol. i, 479) base from the methiodide of α -amino- α -phenylisopropyl alcohol is heated.

The *oxide*, $\begin{matrix} CHPh \\ CHMe \end{matrix} > O$ (yield 40%), is a colourless liquid, b. p. 200°/752 mm., is heavier than water, and has a characteristic odour. J. J. S.

Unsaturated Hydroaromatic Acids with One Semicyclic Double Linking, and Their Derivatives. KARL AUWERS and G. PETERS (*Ber.*, 1910, 43, 3094—3110. Compare this vol. i, 826, 827).—When 1:3-dimethyl- Δ^3 -cyclohexon-5-one is condensed with ethyl bromacetate in presence of zinc and benzene, the product obtained is *ethyl 1:3-dimethyl- Δ^3 -cyclohexene-5-ol-5-acetate*,



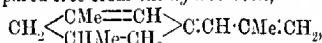
b. p. 110°/2.5 mm. or 123°/4.5 mm. (decomp.), D_4^{25} 1.0126, $n_D^{17.6}$ 1.46857, n_D^{20} 1.47133, n_D^{25} 1.48411 (whence $\Sigma_v = +0.27$, $\Sigma_D = +0.20$, and $\Sigma_v - \Sigma_D = 7\%$), is a colourless, viscid oil, which when heated with dehydrating agents furnishes *ethyl 1:3-dimethyl- Δ^3 -cyclo-*

hexenylidene-5-acetate, $CH_2 < \begin{matrix} CMe=CH \\ CHMe-CH_2 \end{matrix} > C:CH \cdot CO_2Et$, b. p.

111—113°/5.5 mm. or 145—147°/15 mm., D_4^{20} 0.971—0.979, n_D^{20} 1.510—1.513, n_D^{25} 1.516—1.519, $\Sigma_v + 1.79$ to 2.15, $\Sigma_D + 1.87$ to 2.25, and $\Sigma_v - \Sigma_D$ 116 to 123%, which is identical with the substance wrongly assumed by Wallach and Böttcher to be ethyl $\Delta^{1,3}$ -dihydro-3:5-xylol-1-acetate, $CH_2 < \begin{matrix} CMe=CH \\ CHMe-CH \end{matrix} > C \cdot CH_2 \cdot CO_2Et$ (*Abstr.*, 1902, i, 798). On hydrolysis with sodium ethoxide, it yields the free acid,

m. p. 153—154°, and this when heated in closed tubes furnishes the corresponding hydrocarbon, 1:3-dimethyl-5-methylene- Δ^3 -cyclohexene (this vol., i, 826, and Wallach and Böttcher, *loc. cit.*). The acid is reduced with sodium amalgam in presence of carbon dioxide to 1:3-dimethyl- Δ^4 -cyclohexene-5-acetic acid, b. p. 154—155°/16.5 mm., D_4^{20} 0.9947, n_D 1.47428, n_D 1.47731, n_D 1.49068 (whence $\Sigma_a + 0.33$, $\Sigma_b + 0.27$, and $\Sigma_\gamma - \Sigma_c = 8\%$), a colourless oil, which is oxidised by permanganate to an acid, $C_8H_{12}O_3$, and on treatment with bromine followed by sodium hydroxide solution yields *s*-xylylacetic acid.

Ethyl 1:3-dimethyl- Δ^3 -cyclohexenylidene-5-acetate when treated with magnesium methyl iodide yields 1:3-dimethyl- Δ^3 -cyclohexene-5 trimethylcarbinol, $CH_2 \begin{array}{c} \text{CMe}=\text{CH} \\ \text{CHMe-CH}_2 \end{array} \text{C:CH} \cdot \text{CMe}_2 \cdot \text{OH}$, b. p. 125—126°/18 mm., D_4^{20} 0.922—0.934, n_D^{20} 1.503—1.506, n_D 1.508—1.510 (whence $\Sigma_a = +0.95$ to $+1.23$, $\Sigma_b = +1.00$ to 1.28 , and $\Sigma_\gamma - \Sigma_c = 48\%$), which, since it decomposes on heating, could not with certainty be prepared free from the hydrocarbon,



resulting from this decomposition. This hydrocarbon has b. p. 103—106°/17 mm., D_4^{20} 0.862—0.867, n_D^{20} 1.495—1.518, n_D 1.503—1.533, $\Sigma_a + 0.72$ to 1.86 , $\Sigma_b + 0.75$ to 2.02 , and $\Sigma_\gamma - \Sigma_c + 25$ to 93% . T. A. H.

Bismuth Benzoates. GODFRIN (*J. Pharm. Chim.*, 1910, [vii], 2, 385—396. Compare Rebière, *Abstr.*, 1896, ii, 396).—Bismuth benzoate and a series of basic bismuth benzoates are described, full details of their method of preparation being given.

Bismuth benzoate, $Bi(OBz)_3$, prepared by double decomposition between bismuth nitrate and sodium benzoate, both salts being dissolved in a mixture of water and glycerol, and a solution of benzoic acid in water being used for washing and re-crystallising the salt, forms bulky, brilliant, colourless, orthorhombic prisms, is stable up to 140°, and is decomposed by water, alcohol, or ether, forming basic salts. Treated in the cold with twenty times its weight of alcohol it furnishes a salt, $Bi_4O_3(OBz)_6$. This is a dead white powder, seen under the microscope to consist of minute, colourless, cubic crystals. It decomposes at about 160°. When treated with twenty times its weight of cold ether or a like quantity of alcohol at 95°, the neutral salt yields a new basic salt, $Bi_2O_3(BiO \cdot OBz)_{12}$, a white, partly crystalline powder. All the foregoing when treated with alcohol at 95° furnish the salt, $Bi_2O_3(BiO \cdot OBz)_6$, which consists of colourless, microscopic, monoclinic prisms. *Bismuthyl benzoate*, $BiO \cdot OBz$, crystallises in minute, monoclinic prisms. It is stable in air up to 140°, but when treated with alcohol at 95° it decomposes, like the other salts described, furnishing the salt $Bi_2O_3(BiO \cdot OBz)_6$. T. A. H.

Alkylation of Aromatic Amino-acids. IV. Nitroamino- and Iodoamino-acids. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1910, 44, 5, 441—452. Compare this vol. i, 381, 666).—The investigation of the behaviour of aromatic amino-acids on

ethylation is continued by a study of further acids. 4-Nitro-2-aminobenzoic acid gives a mixture of 40% of the primary amino-ester and 40% of the *N*-alkyl acid. 2-Nitro-4-aminobenzoic acid gives only the ester (43.4%). Both 4-iodo-*o*-aminobenzoic acid and 5-iodo-*o*-aminobenzoic acid give only *N*-alkyl acids (71—76%). 4 : 5-Di-iodo-*o*-aminobenzoic acid alkylates with difficulty, and gives only the ester (28%).

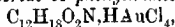
These results show that the tendency of amino-acids to react in an abnormal manner and give esters is not dependent on stereochemical interference.

An improved method for the preparation of 4-nitro-2-aminobenzoic acid is given; the ethyl ester melts at 100°.

4-Iodo-2-nitrobenzoic acid forms prisms, m. p. 192°. 4-Iodo-2-aminobenzoic acid crystallises in flat prisms, decomposing at 268°; 4-iodo-2-ethylaminobenzoic acid forms clusters of plates, m. p. 188°. 4-Iodo-2-methylaminobenzoic acid crystallises in needles, m. p. 197°.

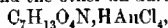
4 : 5-Di-iodo-2-aminobenzoic acid begins to give off iodine at 200°; its ethyl ester forms slender needles, m. p. 137°. N. C.

Complete Methylation of Some Amino-acids. R. ENGELAND (*Ber.*, 1910, 43, 2662—2664. Compare Abstr., 1909, i, 856).—When a mixture of phenylalanine (α -amino- β -phenylpropionic acid), methyl-alcoholic potassium hydroxide, and methyl iodide is boiled gently for several hours, the chief product is *phenyl-N-trimethylalanine methyl ester*, the *platinochloride* of which, $2C_{13}H_{20}O_2NPtCl_6$, has m. p. 177—178°. The *aureichloride* of *phenyltrimethylalanine*,



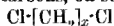
forms golden-yellow needles, m. p. 94—95°.

When α -aminoglutaric acid is treated in a similar manner two products are obtained, the one forms a sparingly soluble *aureichloride*, $C_8H_{12}O_4N_3HAuCl_4$, probably derived from the dimethyl ester of dimethylglutamic acid, and the other an *aureichloride*,



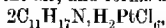
in the form of readily soluble, hygroscopic crystals, probably derived from dimethylglutamic acid. J. J. S.

Synthesis of Compounds of the Normal Phenylpropane, Phenylbutane, and Phenylpentane Series. JULIUS VON BRAUN (*Ber.*, 1910, 43, 2837—2852).—The synthesis of compounds containing the group $C_6H_5 \cdot [CH_2]_x$ is important, since it is very probable that many resins contain such fatty-aromatic chains. Methods based on the interaction of sodium and aryl halides, or of aluminium chloride and aromatic hydrocarbons, on substances of the type

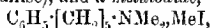


or $Cl \cdot [CH_2]_x \cdot OPh$ have proved unsatisfactory. γ -Bromopropylphthalimide and ϵ -chloroamylphthalimide are very resistant to the attack of sodium, but, contrary to expectation, react with aluminium chloride. The former yields only an additive compound, which is easily decomposed into its generators, but its formation suggests that the usual Friedel-Crafts' reaction might take place with a substance in which the acylated amino-group is removed further from the

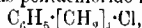
halogen atom. This expectation is fulfilled, benzoyl- ϵ -chloroamylamine and benzoyl- ζ -chlorohexylamine reacting with aluminium chloride and benzene in the usual way. The product of the first reaction is *benzoyl- ϵ -phenylamylamine*, $C_6H_5 \cdot [CH_2]_5 \cdot NHBz$, b. p. 273—275°/15 mm., in 90% yield, which is hydrolysed by hydrochloric acid under pressure to *ϵ -phenylamylamine*, b. p. 131°/15 mm., a colourless liquid which has a faint basic odour, only slowly absorbs water and carbon dioxide from the air, and forms a *platinichloride*,



decomp. 220°, *picrate*, m. p. 152—153°, *benzoyl derivative*, m. p. 66° (the benzoyl derivative, as obtained in the preparation above, has not been made to crystallise), and a *methiodide*,



m. p. 181°, the *platinichloride* of which has m. p. 219°. The normal constitution of the ϵ -phenylamylamine, prepared from benzoyl- ϵ -chloroamylamine by the Friedel-Crafts' method, is proved by the synthesis of the base by the following series of reactions, which represent the fulfilment of the object of the author's work. γ -*Iodopropyl benzene*, $C_6H_5 \cdot [CH_2]_3I$, b. p. 137—140°/20 mm., obtained by the prolonged boiling of γ -chloropropylbenzene and sodium iodide in alcohol, is warmed with an aqueous alcoholic solution of potassium cyanide (2 mols.), whereby γ -*phenylbutyronitrile*, b. p. 142—145°/16 mm., is obtained; the nitrile, by reduction with sodium and alcohol (distilled over sodium and kept for many days, or, better, weeks over calcium), yields δ -*phenylbutylamine*, $C_6H_5 \cdot [CH_2]_4 \cdot NH_2$, b. p. 123—124°/17 mm. (*platinichloride*, decomp. 205°; *picrate*, m. p. 125°; the *N*-*dimethyl methiodide*, $C_6H_5 \cdot [CH_2]_4 \cdot NMe_2 \cdot MeI$, m. p. 191—192°), the *benzoyl derivative* of which, m. p. 83·5°, is converted by distillation with phosphorus pentachloride into δ -*chlorobutylbenzene*,



b. p. 122—123°/17 mm., in 75% yield. This substance, by reactions similar to the preceding, is converted successively into δ -*iodobutylbenzene*, b. p. 148—151°/15 mm., δ -*phenylvaleronitrile*, b. p. 157—161°/17 mm., and ϵ -phenylamylamine, which is identical with the base prepared above.

By distillation with phosphorus pentachloride, benzoyl- ϵ -phenylamylamine yields ϵ -*chloroamylbenzene*, $C_6H_5 \cdot [CH_2]_5Cl$, b. p. 134°/18 mm., which has a very pleasant odour, reacts with alcoholic sodium phenoxide to form *phenyl ϵ -phenylamyl ether*, b. p. 198°/14 mm., and with alcoholic sodium iodide to form ϵ -*iodoamylbenzene*, b. p. 158—165°/20 mm., in which the presence of the normal amyl chain is proved by the reaction of the iodide with alcoholic trimethylamine, whereby ϵ -phenylamyltrimethylammonium iodide, m. p. 181°, is obtained, identical with the salt produced by the exhaustive methylation of ϵ -phenylamylamine.

γ -Chloropropylbenzene is obtained readily from tetrahydroquinoline. The benzoylated base is ruptured by phosphorus pentachloride, and the resulting α - γ -chloropropylbenzanilide is hydrolysed to γ -chloropropylaniline, from which the amino-group is eliminated by diazotisation and subsequent treatment with alkaline stannous chloride. γ -Bromopropylbenzene, which is obtained quantitatively from dihydro-

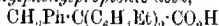
benzyl alcohol and fuming hydrobromic acid at 105°, can only be prepared indirectly from γ -chloropropylbenzene; the latter is boiled for many hours with a large excess of alcoholic sodium phenoxide, and the resulting *phenyl γ -phenylpropyl ether*, $\text{CH}_3\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{OPh}$, b. p. 182—183°/17 mm., is heated with fuming hydrobromic acid.

C. S.

The Liberation of Carbon Monoxide from the Tertiary Acids Arising from the Condensation of Phenylpyruvic Acid with Aromatic Hydrocarbons. AUGUSTIN BISTRZYCKI and LOUIS MAURON (*Ber.*, 1910, 43, 2883—2889. Compare Abstr., 1907, i, 1039; Bistrzycki and von Weber, this vol., i, 742).—The investigation of the liberation of carbon monoxide from tertiary acids on treatment with concentrated sulphuric acid has now been extended to some benzyl-diarylacetic acids, which have now been prepared from phenylpyruvic acid and aromatic hydrocarbons, using cooled, concentrated sulphuric acid as the condensing agent, in the manner previously described (Bistrzycki and Reintke, Abstr., 1905, i, 285). The acids of this type evolve only two-thirds to three-quarters of the theoretical amount of carbon monoxide, the incompleteness of the reaction being due probably to partial sulphonation. The products obtained are completely soluble in water. Triarylethylenes, analogous to the diarylethylenes of Bistrzycki and Reintke (*loc. cit.*), were not obtained. None of the acids loses carbon dioxide on heating.

*β -Phenyl- α -di-*p*-tolylpropionic acid*, $\text{CH}_3\text{Ph} \cdot \text{C}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{CO}_2\text{H}$, from toluene and phenylpyruvic acid, crystallises in colourless, lustrous needles or prisms, m. p. 176°. That the phenylpyruvic acid has not reacted in the desmotropic form (compare Ruhemann and Stapleton, *Trans.*, 1900, 77, 241) follows from the fact that the analogous anisole derivative yields di-*p*-anisyl ketone on oxidation (Lamoni, *Diss.*, Freiburg, Switzerland, 1910, 33). The *silver* salt, $\text{C}_{28}\text{H}_{21}\text{O}_2\text{Ag}$, was obtained as a white precipitate. The *methyl* ester, $\text{C}_{24}\text{H}_{24}\text{O}_2$, forms hexagonal prisms, m. p. 117°.

*α -Phenyl- β -di-*p*-ethylphenylpropionic acid*,



(from ethylbenzene), crystallises in rosettes of stout needles or in flat prisms, m. p. 183—184°. The *ethyl* ester, $\text{C}_{27}\text{H}_{26}\text{O}_2$, forms microscopic prisms, m. p. 61°.

*α -Phenyl- β -di-*o*-xylylpropionic acid*, $\text{CH}_3\text{Ph} \cdot \text{C}(\text{C}_6\text{H}_3\text{Me}_2)_2 \cdot \text{CO}_2\text{H}$ (from *o*-xylene), crystallises in four-sided prisms or in needles, m. p. 160°. The *methyl* ester, $\text{C}_{26}\text{H}_{22}\text{O}_2$, forms microscopic prisms, m. p. 96—97°.

Phenylpyruvic acid does not react with *m*-xylene under the conditions stated, or with mesitylene and naphthalene. Only in one instance was it possible to obtain with benzene an acid of the m. p. of the expected $\alpha\beta$ -triphenylpropionic acid, whilst the products from cumene and cymene were difficult to purify.

R. V. S.

Comparison of Certain Acids Containing a Conjugated System of Double Linkings. ANNIE LOUISE MACLEOD (*Amer. Chem. J.*, 1910, 44, 331—352).—Reimer (Abstr., 1907, i, 852) has

shown that when methyl cinnamylidenemalonate is treated with a Grignard reagent, $\alpha\delta$ -addition takes place, but on decomposing the product rearrangement occurs, and the hydrogen atom by which the magnesium has been replaced is found to occupy the α -position to the carboxyl group. Reimer and Reynolds (Abstr., 1908, i, 988) have shown that methyl α -phenylcinnamylideneacetate reacts less readily with organic magnesium compounds, and that the resulting products consist chiefly of ketones formed by the replacement of the methoxy-group and subsequent addition of a second molecule of the reagent in the $\alpha\delta$ -position. A study has now been made of α -methylcinnamylideneacetic and α -cyanocinnamylideneacetic acids.

α -Methylcinnamylideneacetic acid is pale yellow when first obtained, but becomes white on exposure to light. It has been found that when the yellow form is treated with a very small quantity of sodium amalgam, the yellow colour disappears, and the colourless acid remains. The substance to which the yellow colour is due is therefore present in only small amount, and may possibly be an isomeric form of the acid. When the acid is exposed to direct sunlight for about four days, it is converted into 2:4-diphenylcyclobutane-1:3-di- α -methyl-

acrylic acid, $\text{CO}_2\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CHPh} \end{smallmatrix}\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, m. p.

253—254°, which forms small, transparent prisms, and, on oxidation with potassium permanganate, yields α -truxillic, benzoic, and oxalic acids; its methyl ester, m. p. 126.5—127°, crystallises in slender needles. The acid unites with bromine with formation of a product which appears to be a mixture of a di- and a tetra-bromide; the methyl ester gives a *tetrabromide*, m. p. 200—201°.

When methyl α -methylcinnamylideneacetate is treated with bromine in presence of a little iodine, a *tetrabromide*, m. p. 128°, is produced, whilst, in the absence of iodine, a *dibromide*, m. p. 81°, is obtained, which liberates iodine from alcoholic potassium iodide, thus showing that the bromine atoms are attached to adjacent carbon atoms. When a solution of this dibromide in acetone is oxidised with potassium permanganate in presence of acetic acid, small quantities of a *substance*, m. p. 131°, are produced, which contains halogen, but does not liberate iodine from alcoholic potassium iodide.

Ethyl α -cyanocinnamylideneacetate reacts readily with organic magnesium compounds with production of quantitative yields of $\alpha\delta$ -additive compounds. When this ester (1 mol.) is treated with magnesium ethyl bromide (2½ mols.) and the product is decomposed with hydrochloric acid, ethyl α -cyano- δ -phenyl- β -ethyl- Δ^7 -pentenoate, $\text{CHPh}\cdot\text{CH}\cdot\text{CHEt}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, b. p. 220°/20 mm., is obtained as a yellow oil; on hydrolysis with potassium hydroxide, the *potassium salt* is obtained, from which the *acid* separates on the addition of hydrochloric acid as an uncrystallisable oil. On heating this acid with alcoholic potassium hydroxide for two days, it is converted into δ -phenyl- β -ethylallylmalonic acid,



m. p. 165°, which, when heated above its m. p., yields δ -phenyl- β -ethyl- Δ^7 -pentenoamide, $\text{CHPh}\cdot\text{CH}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 101°, which forms slender needles.

Ethyl α -cyanocinnamylideneacetate reacts with magnesium phenyl bromide to form *ethyl α -cyano- β -diphenyl- Δ^7 -pentenoate*,
 $\text{CHPh}:\text{CH}:\text{CHPh}:\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$,

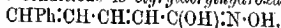
b. p. $263^\circ/18$ mm.

Both α -cyano- and α -methyl-cinnamylideneacetic acids react readily with potassium hydrogen sulphite, yielding colourless, additive compounds which could not be isolated. E. G.

Unsaturated Compounds. VIII. Addition of Hydroxylamine to Unsaturated Acids containing Conjugate Double Linkings. THEODOR POSNER and KARL RONDE (*Ber.*, 1910, 43, 2665—2676. Compare Abstr., 1909, i, 583, 649; Riedel and Schulz, *ibid.*, i, 581).—In further proof of the constitution of β -benzoylamino- β -styrylpropionic [β -benzoylamino- δ -phenyl- Δ^7 -pentenoic] acid is adduced the fact that on oxidation benzoylaspartic acid is formed. Although β -benzoylamino- δ -phenyl- Δ^7 -pentenoic acid and its ester contain olefinic linkings, it has not been found possible to form additive compounds with hydroxylamine or bromine. The addition of hydroxylamine to styrylacrylic acid proceeds slowly, for example, 240 hours' boiling of the solution is required, whereas with cinnamic acid five hours is sufficient.

The addition of hydroxylamine to sorbic, piperic, and α -phenylstyrylacrylic acids and their esters has been studied. The compounds combine with hydroxylamine (compare Riedel and Schulz, *loc. cit.*); sorbic acid at much the same rate as styrylacrylic acid, piperic acid much less readily, as also α -phenylstyrylacrylic acid and all α -alkylated unsaturated acids.

β -Amino- δ -phenyl- Δ^7 -pentenoic acid can be obtained by prolonged boiling of β -hydroxylamino- δ -phenyl- Δ^7 -penteno-hydroxamoxime hydrate (Abstr., 1909, i, 649) with methyl alcohol. It has not been found possible to prepare Riedel and Schulz's β -hydroxylamino- δ -phenyl- Δ^7 -penteno-hydroxamic acid by the method they give; the product formed under these conditions is *styrylacrylhydroxamic acid*,

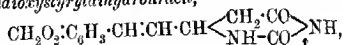


m. p. 146° .

Methyl sorbate, $\text{CHMe}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$, is a colourless liquid with a pleasant odour, and has b. p. $180^\circ/759$ mm. The ester reacts with a cold solution of hydroxylamine in methyl alcohol during the course of a week, yielding an oil which is probably β -hydroxylamino-hydroxosorbhydroxamoxime hydroxide. *Aminohydroxosorbic acid* (β -amino- Δ^7 -hexenoic acid) is formed when the above hydroxide is boiled with methyl alcohol, or when a mixture of the methyl ester and hydroxylamine is boiled for ten hours with methyl alcohol. The same product is also formed when free sorbic acid is used, but the boiling must then be continued for 240 hours; it is an oil, and yields a *benzoyl* derivative, $\text{CHMe}:\text{CH}:\text{CH}(\text{NH}\cdot\text{COPh})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises from alcohol, and has m. p. 152° .

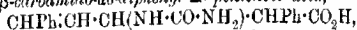
Methyl piperate, $\text{CH}_2\text{O}:\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$, is deposited from methyl alcohol in glistening crystals, m. p. 146° , and reacts with a hot methyl-alcoholic solution of hydroxylamine, yielding β -amino- α -hydropiperic acid (β -amino- δ -3:4-methylenedioxyphenyl- Δ^7 -pentenoic

acid), $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises from water in colourless needles, m. p. 231° (decomp.). A small amount of the same product is also formed when sorbic acid itself is used; it yields a benzoyl derivative, $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}$, m. p. 188° , and reacts with potassium cyanate, forming β -carbamido- α -hydroliperic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, as glistening crystals, m. p. 211° . The carbamido-acid, when heated at 215° , yields 3:4-methylenedioxystyryldihydrouracil,



as a yellow, crystalline powder, m. p. 224° .

Methyl α -phenylstyrylacrylate, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Me}$, forms yellow crystals, m. p. 79 – 80° , and when boiled for several days with hydroxylamine and methyl alcohol yields β -amino- α -diphenyl- Δ^7 -pentenoic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, which crystallises from water in colourless needles, m. p. 200° (decomp.). The benzoyl derivative, $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}$, forms colourless, glistening crystals, m. p. 222 – 5° , and β -carbamido- α -diphenyl- Δ^7 -pentenoic acid,



colourless, glistening needles, m. p. 197° ; the corresponding 5-phenyl-

4-styryldihydrouracil, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\begin{matrix} \text{CHPh}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{matrix}\text{NH}$, forms a pale

yellow powder, m. p. 212 – 5° , after softening at 192° .

When cinnamylidenemalononic acid is heated with methyl alcohol and hydroxylamine, carbon dioxide is evolved, and β -amino- δ -phenyl- Δ^7 -pentenoic acid is formed, whereas the corresponding methyl ester reacts with a methyl-alcoholic solution of hydroxylamine at 0° , yielding a crystalline product, m. p. 72° , which is probably a hydroxylamino-hydroxamoxime hydroxide.

J. J. S.

A New Step in the Reduction of the Nitro-group. III. GUSTAV HELLER and FRIEDRICH FRANTZ (*Ber.*, 1910, 43, 2892–2899. Compare *Abstr.*, 1906, i, 585; 1908, i, 208).—Since in the numerous cases examined it has not been possible to obtain the compound containing a dihydroxylamine group, which is the first product of the reduction of α -nitromandelonitrile, substituted mandelonitriles have now been investigated. Of these, 5-chloro-2-nitromandelonitrile does not yield the characteristic molecular compound in solid form, although its presence in the liquid can be shown by the production of 5-chloroisatin on acetylation. In the case of 5-bromo-2-nitromandelonitrile, the desired substance is obtainable in the form of its hydrochloride, although with a poor yield, and its reactions correspond in all respects with the observations previously recorded. A further proof of the existence of the combination of di- and mono-hydroxylamine compounds follows from the fact that solutions of the above hydrochloride when kept deposit 5-bromo-2-nitrosomandelonitrile, so that evidently no tendency to the formation of an azoxy-compound exists.

5-Chloro-2-nitromandelonitrile, $\text{C}_8\text{H}_5\text{O}_3\text{N}_2\text{Cl}$, is prepared by adding a concentrated, aqueous solution of potassium cyanide to a solution of 5-chloro-2-nitrobenzaldehyde (Einhorn and Eichengrün, *Abstr.*, 1891, 1098) in glacial acetic acid, or by adding the aldehyde to twice its weight of anhydrous hydrocyanic acid. It forms rosettes

of needles, m. p. 85° , and also large prisms containing chloroform of crystallisation, m. p. $64-66^{\circ}$.

5-chloro-2-nitromandelic acid, $C_8H_6O_5NCl$, m. p. 134° , is obtained by evaporating the nitrile with twenty times its weight of hydrochloric acid almost to dryness. The methyl ester, $C_9H_7O_5NCl$, has m. p. $87-88^{\circ}$. With alcoholic ammonia, 5-chloro-2-nitromandelonitrile yields the ammonium salt of 5-chloro-2-nitrosobenzoic acid, which may be obtained from it by the action of dilute hydrochloric acid. The free acid crystallises in colourless needles, which become coloured towards 170° and melt at 179° . After reduction with zinc and acetic acid no precipitate was observed, but on addition of hydrochloric acid and acetic anhydride a dark-coloured oil separated, and the solution when kept yielded 5-chloroisatin. The oil was insoluble in cold sodium hydroxide, and therefore was not 5-chloro-*N*-acetoxyisatin.

5-bromo-2-nitromandelonitrile, prepared from 5-bromo-2-nitrobenzaldehyde, has m. p. 81° . When it is reduced with zinc and acetic acid in an atmosphere of hydrogen, the liquid being cooled with water and well stirred, the molecular compound of 5-bromo-2-mono- and 5-bromo-2-dihydroxylaminomandelonitrile hydrochloride, $C_{16}H_{10}O_5N_4Cl_2Br_2$, separates. After purification by precipitation with concentrated hydrochloric acid from solution in weaker acid, it crystallises in a mass of colourless, crooked needles, which become coloured at 130° and decompose towards 145° . The free compound can also be isolated. On keeping, an aqueous solution of the hydrochloride deposits a brown precipitate, which, when saponified with dilute sodium hydroxide, yields bromoanthroxanic acid and bromoisatin. These substances are obtained directly by heating the salt with concentrated hydrochloric acid. *5-Bromoisatin*, $C_8H_5O_2NBr$, forms yellow needles, m. p. 255° . *5-Bromoanthroxanic acid*, $C_8H_4O_5NBr$, crystallises in colourless needles. It melts at $202-203^{\circ}$, with evolution of gas and partial sublimation; the yellow residue darkens on further heating, and melts towards 253° with evolution of gas. Bromoanthroxanic acid is reduced by ammoniacal ferrous sulphate, and on acidification 5-bromoisatin is precipitated. The hydrochloride of the molecular compound yields on treatment with dilute sodium hydroxide a colourless compound, m. p. $186-187^{\circ}$, and an aminocarboxylic acid, probably 5-bromo-2-amino-mandelic acid, crystallising in colourless needles, which become coloured towards 230° . Acetylation of the molecular compound in presence of an excess of hydrochloric acid gives rise to 5-bromo-1-acetoxyisatin. Phenylhydrazine reacts with the hydrochloride, yielding 5-bromo-1-hydroxyisatinphenylhydrazone and 5-bromo-isatin-2-phenylhydrazone, $C_{11}H_{10}ON_3Br$, which forms dark red crystals, m. p. $242-243^{\circ}$.

5-Bromo-2-nitrosomandelonitrile, $C_8H_5O_2N_2Br$, which can be obtained (in addition to 5-bromoisatin) from the filtrate from the molecular compound in the preparation of the latter, crystallises in compact, colourless prisms, m. p. $225-226^{\circ}$. On hydrolysis it yields 5-bromoanthroxanic acid.

R. V. S.

Action of Amines on Phthalic Acid. VII. J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1910, 32, 1319-1330).—In continuation of the work on the interaction of amines with phthalic

acid and its derivatives (Abstr., 1907, i, 692, 1044; 1909, i, 28, 798, 909; this vol., i, 263), a study has been made of phthalamic acids containing one or more chlorine atoms or nitro-groups in the benzene nucleus.

Di-m-toluidine and *di-p-chloroaniline* 3:6-dichlorophthalates, m. p. 176° and 215° respectively, form pale yellow crystals. An improved method is described for the preparation of 3:6-dichlorophthalanic acid and its anil. The anil has m. p. 201°, and not 191° as stated by Graebe (Abstr., 1900, i, 547). The acid is not affected by solutions of amines in benzene, but is readily converted into the anil by the action of 50% alcohol. This dehydrating action of alcohol has been discussed by Tingle and Rolker (Abstr., 1909, i, 29).

Tetrachlorophthal-o-toluidic acid, $C_6H_4Me \cdot NH \cdot CO \cdot C_6H_2Cl_4 \cdot CO_2H$, m. p. 218—220°, obtained by the action of *o*-toluidine on tetrachlorophthalic acid or anhydride, forms white, lustrous crystals.

Tetrachlorophthalanic acid, $NHPh \cdot CO \cdot C_6Cl_4 \cdot CO_2H$, m. p. 266°, obtained by boiling tetrachlorophthalanil (Graebe and Buenzod, Abstr., 1899, i, 763) with solution of potassium hydroxide or by the action of aniline on tetrachlorophthalic anhydride, forms white crystals; its sodium and potassium salts are colloidal, and yield soapy solutions. *Tetrachlorophthal-β-naphthylamic acid*, $C_{10}H_7 \cdot NH \cdot CO \cdot C_6Cl_4 \cdot CO_2H$, m. p. 287°, forms white crystals, and yields colloidal sodium and potassium salts. When the acid is heated for ten minutes at 260—270°, it is converted into the *β-naphthylimide*, $C_6Cl_4 \cdot \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ N \cdot C_{10}H_7 \end{smallmatrix} \cdot CO$, m. p. 287°, which is a white, crystalline substance.

When 3-nitrophthalanic acid, $NHPh \cdot CO \cdot C_6H_3(NO_2) \cdot CO_2H$, is heated at 100° with 50% alcohol, it is slowly transformed into a 3-nitrophthalodianilide, m. p. 233—234°, which appears to be isomeric with that obtained by Chambers (Abstr., 1903, i, 699) of m. p. 211—212°. 3-Nitrophthal-β-naphthylamic acid,

$C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_3(NO_2) \cdot CO_2H$, m. p. 201—202°, obtained by the action of β-naphthylamine on 3-nitrophthalic anhydride, forms light yellow crystals.

4-Nitrophthalanic acid, obtained by heating the anil (Graebe and Buenzod, *loc. cit.*) with solution of potassium hydroxide or by treating aniline with 4-nitrophthalic anhydride, has m. p. 192°, and not 181° as stated by Bogert (Abstr., 1902, i, 98). The anil has m. p. 200—201° (Bogert gives 194°). When 4-nitrophthalanic acid is heated at 100° with 50% alcohol, it is partly transformed into the anil; in presence of aniline the same product is obtained, together with a small quantity of a compound, m. p. 199—200°, which is probably 4-nitrophthalodianilide, $NO_2 \cdot C_6H_3(CO \cdot NHPh)_2$.

On comparing the results of the transformation experiments with 3- and 4-nitrophthalanic acids, it is evident that the approximation of negative groups ($CO_2H \cdot CO_2H \cdot NO_2 = 1 : 2 : 3$) inhibits the formation of the anil and greatly favours that of the dianilide, whereas the reverse is the case when the nitro-group is in the 4-position. 4-Nitrophthal-β-naphthylamic acid, $C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_3(NO_2) \cdot CO_2H$, m. p. 202—204°, prepared by the action of β-naphthylamine on 4-nitrophthalic anhydride, forms pale yellow crystals.

Camphoro-β-naphthylamic acid, $C_{10}H_7 \cdot NH \cdot CO \cdot C_8H_{14} \cdot CO_2H$, m. p. 220—221°, obtained by the action of β-naphthylamine on camphoric anhydride, and camphoranilic acid (Auwers, Abstr., 1900, i, 85) are not affected by prolonged heating with amines or with 50% alcohol.

E. G.

Synthesis of Ethyl cyclobutanehexacarboxylate. YUGI SHIBATA (*Ber.*, 1910, 43, 2619—2622).—Ethyl cyclobutanehexacarboxylate, $(CO_2Et)_2C \begin{smallmatrix} \diagup C(CO_2Et)_2 \\ \diagdown CH(CO_2Et) \end{smallmatrix} CH \cdot CO_2Et$, can be synthesised by the action of the disodium derivative of ethyl ethanetetracarboxylate (Bischoff and Rach, Abstr., 1885, 244) on ethyl dibromosuccinate (Gorodetzky, Abstr., 1888, 820) in the presence of dry ether at 0° and with vigorous automatic stirring. It crystallises from alcohol in large, monoelonic plates [$a:b:c = 1.565:1:1.542$; $\beta = 131^\circ 32'$], m. p. 80°. Unaltered ethyl ethanetetracarboxylate is deposited with the cyclobutane derivative, but can be removed mechanically, as it forms large, needle-shaped crystals.

An oily by-product formed during the condensation is Bischoff's ethyl ethylencetetracarboxylate, $C(CO_2Et)_2 \cdot C(CO_2Et)_2$. The condensation does not take place when the reagents are heated in sealed tubes at 120—130°, and the same products are formed when ethyl isodibromosuccinate is used.

J. J. S.

Rotatory Power of Usnic Acid and other Lichen Derivatives. III. HEINRICH SALKOWSKI (*Annalen*, 1910, 377, 123—126, Compare Abstr., 1901, i, 152; 1902, i, 228).—The values for $[\alpha]_D^{20}$ for the following substances are given: *d*-Usnic acid (from nineteen species of lichens), +461.9° to +521.9°; *l*-usnic acid (from thirteen species), -455.9° to -496.8°; kamschadalic acid, +26.42°; lepranthin, +70.5°; pleopsidic acid, -66.15°; protolichenosteric acid, +12.1°.

Barbatie acid, lecanarolic acid, and salazinic acid appear to be inactive.

In most cases chloroform solutions were used.

Gymnogrammen from *Gymnogramme chrysophylla* has an orange colour, m. p. 159°, and $[\alpha]_D^{20} + 12^\circ$.

J. J. S.

Ethyl Tannate. RODGER J. MANSING (*J. Amer. Chem. Soc.*, 1910, 32, 1312—1319).—The composition of gallotannic acid has hitherto been uncertain, owing to the fact that crystalline derivatives were not known, and the substance was therefore difficult to purify. The ethyl ester has now been prepared in two crystalline forms with different amounts of water of crystallisation.

On treating an alcoholic solution of gallotannic acid with dry hydrogen chloride, ethyl gallotannate, $C_{51}H_{22}O_{20} \cdot 5H_2O$, m. p. 157°, is obtained in the form of nodules of pale yellow, lustrous crystals. When hydrolysed with dilute hydrochloric acid or dilute potassium hydroxide, it yields ethyl alcohol, dextrose, and gallic acid. Estimations of the gallic acid and dextrose, and determinations of the molecular

weight by the ebullioscopic method have shown that ethyl gallotannate has the composition $C_{41}H_{27}O_{21}(OEt)_5 \cdot 5H_2O$, and that it is a glucoside in which one formula weight of dextrose and five formula weights of gallic acid are represented in one molecule of the ester. Gallotannic acid is therefore represented by the formula $C_{41}H_{27}O_{21}(OH)_5$.

The ester was synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

If a saturated solution of the ester is allowed to evaporate at the ordinary temperature, large, pale brown crystals are obtained of the composition $C_{51}H_{52}O_{26} \cdot 15H_2O$, m. p. 132° . F. G.

Theory of the Phenomena of Halochromy. I. Additive Compounds of Tin Halogenides and Carbonyl Compounds PAUL PFEIFFER [with O. HALPERIN, E. PROS, and V. SCHWARZKOPF] (*Annalen*, 1910, 376, 285—310).—The first step in the elucidation of the constitution of the coloured additive compounds of organic substances and metallic salts and acids, and therewith the nature of the phenomenon of halochromy, must be a systematic examination of the additive capacity of simply constituted substances. Since halochromy is most frequently observed in connexion with carbonyl compounds, these have been selected as the organic components; the inorganic are tin tetrachloride and tetrabromide, which have the property of forming well-characterised molecular compounds of simple composition.

The additive compound is obtained by bringing the tin halogenide and the carbonyl compound (aldehyde, ketone, acid, ester, or amide, containing generally the benzoyl or cinnamoyl group; acid chloride do not form additive compounds) together in anhydrous ether, benzene, or chloroform; in the case of liquid esters, a solvent is dispensed with. In this way have been prepared the following colourless compounds: $SnCl_4 \cdot 2PhCHO$, m. p. $187-189^\circ$; $SnBr_4 \cdot 2PhCHO$, m. p. $127-128^\circ$; $SnCl_4 \cdot 2CHPh \cdot CH : CH \cdot CHO$, m. p. $225-230^\circ$;

$SnBr_4 \cdot 2CHPh \cdot CH : CH \cdot CHO$,
m. p. 195° ; $SnCl_4 \cdot 2(p)OH \cdot C_6H_4 \cdot CHO$, m. p. 185° ;

$SnCl_4 \cdot 2(p)OMe \cdot C_6H_4 \cdot CHO$,
m. p. 158° ; $SnCl_4 \cdot 2COPhMe$, m. p. $131-133^\circ$; $SnCl_4 \cdot 2Ph \cdot CO \cdot Et$,
m. p. 40° ; $SnCl_4 \cdot 2(p)C_6H_4 \cdot Me \cdot CO_2Et$; $SnCl_4 \cdot 2CHPh \cdot CH : CH \cdot CO \cdot Et$,
m. p. 134° ; $SnBr_4 \cdot 2(o)OH \cdot C_6H_4 \cdot CO_2Me \cdot 2H_2O$, m. p. $67-68^\circ$.
 $SnCl_4 \cdot 2Ph \cdot CO_2H$, m. p. about 90° ; $SnCl_4 \cdot 2CHPh \cdot CH : CH \cdot CO_2H$,
m. p. $85-112^\circ$; $SnCl_4 \cdot 2Ph \cdot CO \cdot NH_2$, m. p. about 227° ;

$SnCl_4 \cdot 2CHPh \cdot CH : CH \cdot CO \cdot NH_2$,
m. p. $238-239^\circ$; $SnCl_4 \cdot 2(o)OH \cdot C_6H_4 \cdot CO \cdot NH_2$, m. p. 203° ; and also
the following, which are yellow or yellowish: $SnCl_4 \cdot 2C_4H_9 \cdot CHO$,
unstable; $SnBr_4 \cdot 2(p)OH \cdot C_6H_4 \cdot CHO$, m. p. 154° ;

$SnCl_4 \cdot 2CHPh \cdot CH : CH \cdot COMe$,
m. p. 120° . All these compounds are decomposed by water, and contain 1 molecule of the inorganic to 2 of the organic component. Their composition may be represented, therefore, by the general expression $SnX_4 \cdot 2R \cdot CO \cdot A$, where X is chlorine or bromine, R is Ph , C_6H_4 , OH , $C_6H_4 \cdot OMe$, $CHPh \cdot CH$, or C_4H_9 , and A is H , Me .

(OH, OEt, or NH_2). The common constituent of all these compounds is the carbonyl group, which therefore is the means by which the organic and the inorganic components are linked. The co-ordination number of tin is six. Moreover, additive compounds of the tin series are formed, almost without exception, extra-molecularly, not intra-molecularly. Therefore the two organic molecules of the additive compound probably occupy the two free co-ordination positions of the SnX_4 molecule, being linked by the oxygen, since tin has a much greater affinity for oxygen than for carbon. These views lead to the constitution $\text{X}_4\text{Sn} \begin{smallmatrix} \nearrow \text{O:CRA} \\ \searrow \text{O:CRA} \end{smallmatrix}$ for the preceding additive compounds.

These views, in conjunction with Thiele's theory, are utilised by the author to explain the facts that in a compound containing an unsaturated group the saturation of this group tends to diminish the colour intensity, whilst by the formation of a molecular additive compound colour is produced or intensified. For example, a substance,

$\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix} > \text{C}=\text{O}$, in virtue of the residual affinities of the carbon and oxygen atoms, is converted by the addition of $\text{Y}\cdot\text{Y}$ into a more saturated system, $\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix} > \text{CY}\cdot\text{OY}$, with a corresponding diminution or loss of colour;

this is not surprising, because, according to modern views, the colour of purely organic substances is due primarily to the presence of unsaturated groups. When, however, an extramolecular additive compound, such as those above, is formed by a neutralisation of the residual affinity of the oxygen atom only, the unsaturated carbon atom acquires a more pronounced unsaturated character, approximating to that of tervalent carbon, and therefore may be regarded as a specific chromophore, and the additive compound, under suitable circumstances, may be coloured or exhibit halochromy.

In the author's opinion the action of catalysts in hydrolysis, esterification, ketone-synthesis, etc., may be explained by the initial formation of a molecular compound of the catalyst and the organic substance at its carbonyl oxygen atom. C. S.

Action of Chloride of Sulphur and of Sulphuryl Chloride on Piperonal. KARL WEISSE (*Ber.*, 1910, 43, 2605—2606. Compare D.R.-P. 165727).—Piperonal reacts to only a slight extent when distilled with sulphuryl chloride, but when a mixture of the two compounds is kept at the ordinary temperature for two days a good yield of *chloropiperonal*, $\text{C}_8\text{H}_5\text{O}_3\text{Cl}$, is obtained; it crystallises from alcohol in brilliant needles, m. p. 114—115°.

When this chloro-derivative is heated with chloride of sulphur at 150° for an hour, and then at 130° for three hours, a resinous product is obtained, which loses carbon dioxide when heated, forming *chloroprotocatechualdehyde*, $\text{C}_7\text{H}_5\text{O}_3\text{Cl}$, m. p. 211°.

Chloroprotocatechualdehyde reacts with an alcoholic potassium hydroxide solution of ethyl chlorocarbonate, yielding the *ethyl carbonate* derivative, $\text{C}_{10}\text{H}_9\text{O}_5\text{Cl}$, which crystallises from water in glistening plates, m. p. 135°.

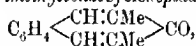
J. J. S.

Condensation Products of *o*-Phthalaldehyde. III. JOHANNES THIELE and ERNST WEITZ (*Annalen*, 1910, 377, 1—22. Compare Thiele and Falk, *Abstr.*, 1906, i, 750; Thiele and Schneider, *Abstr.*, 1909, i, 929).—Ketones with the grouping $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ can react with *o*-phthalaldehyde in two distinct ways: (a) formation of a hydrindone derivative, as in the case of acetone or acetophenone; (b) formation of a benzocycloheptadienone, as in the case of diethyl ketone.

It is shown that methyl ketones which contain a normal carbon chain react according to the latter scheme; thus methyl ethyl, methyl propyl, and methyl *n*-butyl ketones yield respectively methyl-, ethyl-, and propyl-benzocycloheptadienones, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH:CR} \\ \text{CH:CH} \end{smallmatrix}\rangle\text{CO}$. Naphthalene derivatives do not appear to be formed, but small amounts of acylhydrindones can be detected among the condensation products. Methyl isobutyl ketone yields as chief condensation product isovalerylhydrindone, and practically no isopropylbenzocycloheptadienone. Methyl isopropyl ketone yields isobutyrylhydrindone, as there is no methylene group present capable of yielding a benzocycloheptadienone derivative.

Phthalaldehyde also condenses readily with nitromethane, yielding nitrohydrindone, which reacts in the enolic form, nitrohydroxyhydrindene, as it yields an acetyl derivative and a methyl ether. Its constitution has been determined by conversion into Gabriel's amino hydrindone.

Benzocycloheptadienone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix}\rangle\text{CO}$, prepared by heating the carboxylic acid (*Abstr.*, 1909, i, 930) with 0.5% hydrochloric acid at 200° for four to five hours, crystallises from light petroleum in pale yellow plates, m. p. 66—67°, and does not react with phenylhydrazine or hydroxylamine. The dibromide, $\text{C}_{11}\text{H}_{18}\text{OBr}_2$, forms colourless needles, m. p. 204°. Dimethylbenzocycloheptadienone,



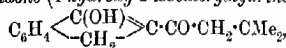
prepared from diethyl ketone and phthalaldehyde in the presence of methyl-alcoholic potassium hydroxide solution, crystallises from dilute alcohol in colourless plates, m. p. 85°; diphenylbenzocycloheptadienone, $\text{C}_{23}\text{H}_{18}\text{O}$, obtained when dibenzyl ketone is used, crystallises in pale yellow prisms, m. p. 118.5°, and does not yield a dibromide; methylbenzocycloheptadienone, $\text{C}_{13}\text{H}_{10}\text{O}$, crystallises from light petroleum (40—70°) in felted needles, m. p. 61°; the corresponding ethyl derivative, $\text{C}_{13}\text{H}_{12}\text{O}$, has m. p. 42—43°, and the *n*-propyl derivative, $\text{C}_{14}\text{H}_{14}\text{O}$, has b. p. 188°/13 mm., and solidifies when kept in a freezing mixture.

Diphenylmethylbenzocycloheptanone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CHPh} \\ \text{CH}_2\cdot\text{CHPh} \end{smallmatrix}\rangle\text{CO}$, prepared by reducing the corresponding dienone with sodium amalgam and alcohol in the presence of acetic acid, crystallises from 75% alcohol in colourless needles, m. p. 158°. The ketone does not react with phenylhydrazine or semicarbazide, but with magnesium methyl iodide yields diphenylmethylbenzocycloheptanol, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CHPh} \\ \text{CH}_2\cdot\text{CHPh} \end{smallmatrix}\rangle\text{CMe}\cdot\text{OH}$, which

forms colourless crystals, m. p. 211° , and is stable towards permanganate.

Dimethylbenzocycloheptanol, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH} \cdot \text{OH}$, obtained by reducing the corresponding dienone, crystallises from dilute alcohol in colourless needles, m. p. $123-124^{\circ}$, and yields an *acetyl* derivative, m. p. 141° . *Diphenylbenzocycloheptanol*, $C_{22}H_{22}O$, forms colourless plates, m. p. 160° . *Benzocycloheptanol*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{OH}$, prepared from benzocycloheptadienone, has m. p. about 80° .

isobutyrylhydrindone (1-hydroxy-2-isobutyrylhydrindene),



crystallises from methyl alcohol in needles, soluble in alkalis, and gives a red to reddish-violet coloration with ferric chloride. When a small amount of alkali is used in the condensation, much phenylnaphthylene ketone is formed. *isobutyrylhydrindone* (1-hydroxy-2-isobutyrylhydrindene), $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{CHMe}_2$, has b. p. $170-174^{\circ}/13-14 \text{ mm.}$, and m. p. $35-36^{\circ}$.

2-Nitro-1-hydrindone (2-nitroindanol), $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{NO}_2$, crystallises from light petroleum (100°) in slender, sulphur-yellow needles, m. p. about 117° (decomp.). It dissolves in alkali hydroxide solutions and is decomposed when boiled with water. The *acetyl* derivative, $C_{11}H_9O_4N$, crystallises in slender, yellow needles, turns dark coloured at $108-109^{\circ}$, melts and decomposes above 120° , and yields a *dibromide*, $C_{11}H_7O_4NBr_2$, in the form of colourless, compact crystals, m. p. 136° . The *methyl ether* of the nitro-derivative, $C_9H_9O_3N$, is obtained readily from the acetyl derivative by the action of methyl alcohol and hydrogen chloride; it crystallises in pale yellow plates, m. p. 83° .

Hydrobenzoin-o-dialdehyde, $\text{CHO} \cdot C_6H_4 \cdot \text{CH(OH)} \cdot \text{CH(OH)} \cdot C_6H_4 \cdot \text{CHO}$, prepared by reducing phthalaldehyde with zinc dust in the presence of alcohol and glacial acetic acid at the ordinary temperature, crystallises from alcohol in minute needles, m. p. $176-177^{\circ}$. Its solution in concentrated sulphuric acid has an intense yellow colour with a greenish-yellow fluorescence. Its *phenylhydrazine*, $C_{25}H_{20}O_4N_4$, crystallises from aniline, and has m. p. above 260° . When oxidised with nitric acid the dialdehyde yields hydrodiphthalyl (compare Hasselbach, Abstr., 1888, 485), but with alkaline permanganate yields benzil-o-dicarboxylic acid (Graebe, Abstr., 1888, 1095; 1890, 989). Concentrated sulphuric acid reacts with a solution of the dialdehyde in glacial acetic acid, yielding 2-o-aldehydophenyl-3-indone, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CH} \end{smallmatrix} \text{C} \cdot C_6H_4 \cdot \text{CHO}$, which crystallises from alcohol in brilliant, orange-red needles, m. p. 141° . An amorphous by-product is formed at the same time, and the amount of this increases if the reaction mixture is heated for some time. The indone derivative reduces ammoniacal silver nitrate solution and also alkaline permanganate, and yields a *dibromide*, $C_{16}H_{10}O_2Br_2$, m. p. above 246° . A small amount of this indone is formed in the preparation of phthalaldehyde.

J. J. S.

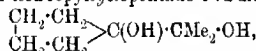
Synthesis of Ketones, in the Tetrahydroaromatic Series. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1910, 151, 758—759).—This paper contains an account of further applications of the general reaction already described (this vol., i, 322) to cyclohexene. By treating this hydrocarbon with *n*-butyryl chloride in presence of aluminium chloride, a condensation product is obtained, which loses hydrogen chloride when heated with diethylamine, forming *n*-butyrylcyclohexene, $C_3H_7 \cdot CO \cdot C_6H_{10}$, b. p. 225—226°, 113—114°/7 mm.; the semicarbazone has m. p. 171°. isobutyrylcyclohexene has b. p. 233°, 128—130°/7 mm.; the semicarbazone has m. p. 180°. Heptylcyclohexene has b. p. 274—275°, 140—141°/5 mm.; the semicarbazone has m. p. 145°. Laurylcyclohexene, b. p. 342—343°, 209—211°/6 mm., forms a semicarbazone, m. p. 125°.

The foregoing ketones may be utilised for the production of hexa-hydroaromatic ketones, the reduction being effected by catalytic hydrogenation in presence of reduced nickel.

By condensing tetrahydroacetophenone with ethyl chloroacetate in presence of sodium ethoxide, ethyl methylcyclohexenylglycidate, $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CMe \cdot C_6H_9 \\ CH \cdot CO_2Et \end{smallmatrix}$, has been obtained. This substance has b. p. 145—146°/14 mm., and on hydrolysis gives an unstable acid, which loses carbon dioxide when heated in a vacuum, forming tetrahydroatropaldehyde, $C_6H_9 \cdot CHMe \cdot CHO$, b. p. 90—93°/15 mm.

W. O. W.

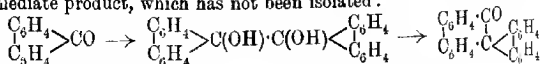
The Pinacone Transformation in the Case of Cyclic Compounds. I. HANS MEERWEIN and WALTER UNSKEL (*Annalen*, 1910, 376, 152—153).—1-isopropylcyclopentane-1 : α -diol,



prepared by the action of magnesium methyl iodide on methyl α -hydroxycyclopentanecarboxylate, readily undergoes the pinacone transformation when heated with dilute sulphuric or oxalic acid.

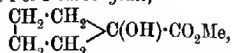
An intermediate product is probably the oxide, $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad | \\ CH_3 \cdot CH_2 \end{array} > C \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CMe_2 \\ O \end{smallmatrix}$, but the final product isolated is 1 : 1-dimethylcyclohexan-6-one, the constitution of which was determined by oxidation to *aa*-dimethyladipic acid by means of nitric acid. The reaction (cyclic pinacone transformation) consists in the conversion of a 5-carbon into a 6-carbon ring, and is of interest as bearing on certain transformations in the terpene series.

Reactions of the same type are the conversion of pulegonic acid (isopropylidenemethylcyclopentanecarboxylic acid) into pulenone (1 : 4 : 4-trimethylcyclohexan-5-one) (compare Wallach, *Abstr.*, 1904, i, 74); also the conversion of dicyclopentanepinacone into 1 : 1-tetramethylenecyclohexan-2-one (Meiser, *Abstr.*, 1899, i, 742), and the transformation of fluorenone into a phenanthrene derivative when reduced with zinc and acetyl chloride, a pinacone being the intermediate product, which has not been isolated :



(compare Klinger and Lonnes, *Abstr.*, 1896, i, 691).

Methyl cyclopentan-1-ol-1-carboxylate,



is readily prepared from the acid (Gärtner, Abstr., 1893, i, 557) by the usual method. It has b. p. $87^\circ/23$ mm., or $84^\circ/16$ mm. 1-iso*Propylcyclopentane-1:α-diol*, $\text{C}_8\text{H}_{16}\text{O}_2$, crystallises from light petroleum in glistening, colourless prisms, m. p. 62° , and b. p. $105\text{--}110^\circ/15$ mm.

1:1-*Dimethylcyclohexan-6-one*, $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CMe}_2$, is a colourless oil, and yields a *semicarbazone*, $\text{C}_{10}\text{H}_{17}\text{ON}_3$, which crystallises in large, flat needles, m. p. $196\text{--}197^\circ$. The pure ketone, prepared by hydrolysing the semicarbazone with 10% sulphuric acid, has b. p. $59\text{--}61^\circ/14$ mm. or $170\text{--}2\text{--}170\text{--}4^\circ/758$ mm., D_{20}^{20} 0.9194, and n_D^{20} 1.44744, and has an odour of camphor and menthone.

A small amount of an unsaturated hydrocarbon accompanies the crude ketone.

J. J. S.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds Containing Alkyloxy-groups. GRACE POTTER REYNOLDS (*Amer. Chem. J.*, 1910, 44, 305—331).—The reactions between organic magnesium compounds and unsaturated compounds have been studied by Kohler (Abstr., 1905, i, 208; 1907, i, 139, 1050) with special reference to the effect of hydrocarbon residues in substances containing the chain $\text{C}:\text{C}:\text{C}:\text{O}$, as the result of which it is possible to predict the mode of addition of a magnesium compound to such a substance. It has also been shown that in the reactions with ethyl α -cyanocinnamate (Abstr., 1905, i, 347) and ethyl benzylidenemalonate (Abstr., 1905, i, 700) the presence of the cyano- and carbethoxy-groups in the α -position prevents the replacement of the alkyloxy-group, and therefore only *additive* products are obtained. In continuation of this work, an investigation has been made of the influence of alkyloxy-groups on the mode of addition. An attempt has been made to use the Grignard reagent for the study of keto-enol-tautomerism, but it has been found to be unsuitable for the purpose.

Magnesium methyl iodide reacts instantaneously with phenyl formylethyl ketone when dissolved in ethyl ether, but does not react with it in an amyl ether solution, and it is therefore evident that the method cannot be used for the estimation of the hydroxyl group in this ketone (compare Hibbert and Sudborough, *Trans.*, 1904, 85, 933, and Zerewitinoff, Abstr., 1907, ii, 509).

Ethyl hydroxymethylenemalonate and phenyl formylethyl ketone were selected for the experiments to ascertain whether the nature of the products obtained in the Grignard reaction can serve for the estimation of the relative amounts of ketonic and enolic modifications. Magnesium phenyl bromide reacts with ethyl hydroxymethylenemalonate to form a product, which, when decomposed in the usual way, yields ethyl benzylidenemalonate. Magnesium ethyl bromide also reacts with ethyl hydroxymethylenemalonate, but the product could not be identified.

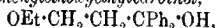
Ethyl α-phenylpropylmalonate, $\text{CHPhEt}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. 187–188°/22 mm., prepared by the action of magnesium ethyl bromide on ethyl benzylidenemalonate, is a colourless liquid; the corresponding acid, m. p. 74°, crystallises with $1\text{H}_2\text{O}$.

Magnesium phenyl bromide reacts with phenyl formylethyl ketone to form a product which yields benzylidenepropiophenone. With magnesium ethyl bromide a substance was obtained consisting of impure phenyl α-methylbutenyl ketone, which was identified by means of its *dibromide*, m. p. 67°, and also by its conversion into phenyl β-phenyl-α-methylbutyl ketone by the action of magnesium phenyl bromide. *Phenyl β-phenyl-α-methylbutyl ketone*,
 $\text{CHPhEt}\cdot\text{CHMe}\cdot\text{COPh}$,

m. p. 60·5°, prepared by the action of magnesium ethyl bromide on benzylidenepropiophenone, forms white, slender needles; its *oxime* has m. p. 119°.

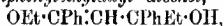
Ethyl ethoxymethylenemalonate reacts with magnesium phenyl bromide with formation of a product which yields ethyl diphenylmethylmalonate; on treating this ester with alcoholic potassium hydroxide, *potassium ethyl diphenylmethylmalonate* is obtained. When ethyl ethoxymethylenemalonate is treated with magnesium ethyl bromide, *ethyl α-ethylpropylmalonate*, $\text{CHEt}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. 138°/21 mm., is obtained as a colourless, mobile liquid.

β-Ethoxypropiophenone reacts with magnesium phenyl bromide with formation of *diphenylethoxyethylcarbinol*,



h. p. 207°/21 mm., m. p. 78°, which crystallises in white plates. This ketone also reacts with magnesium ethyl bromide with production of *phenylethylethoxyethylcarbinol*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CPhEt}\cdot\text{OH}$, b. p. 151°/24 mm., as a colourless, mobile liquid.

Phenyl β-ethoxystyryl ketone can be obtained in fair yield by boiling phenyl dibromostyryl ketone with sodium ethoxide. This ketone reacts with magnesium ethyl bromide in presence of the usual quantity of ether to form a product, which, when decomposed with hydrochloric acid at 0°, yielded ethoxydiphenylethylalyl alcohol, together with ethoxyphenylethylpropiophenone and two solid compounds, $\text{C}_{34}\text{H}_{32}\text{O}_3$, one of which has m. p. 205° and forms white needles, whilst the other has m. p. 185° and forms yellow needles; the white substance slowly changes in solution into the yellow compound. *Ethoxydiphenylethylalyl alcohol*,



m. p. 60·5°, crystallises in white, slender needles. *Ethoxyphenylethylpropiophenone*, $\text{OEt}\cdot\text{CPhEt}\cdot\text{CH}_2\cdot\text{COPh}$, b. p. 96°/18 mm., is a colourless, mobile liquid; its *semicarbazide-semicarbazone* has m. p. 161°. In another experiment on the action of magnesium ethyl bromide on phenyl β-ethoxystyryl ketone, a much larger quantity of ether was used, and, on decomposing the product, the same three solid compounds were obtained, together with *γ-diphenyl-Δ^{8,8}-heptadiene*, $\text{CPhEt}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CHMe}$, b. p. 191–195°/20 mm., as a colourless liquid. When phenyl β-ethoxystyryl ketone is added to magnesium phenyl bromide in presence of a large quantity of ether, and the product is decomposed in the usual way, tetraphenylalyl alcohol is

obtained, but if the reaction is carried out in presence of only the usual quantity of ether, *ethoxytriphenylallyl alcohol*,

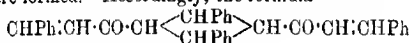


m. p. 120.5° , is produced, which crystallises in white, slender needles.

These experiments with phenyl β -ethoxystyryl ketone show that in the reaction between organic magnesium compounds and unsaturated compounds having an alkyloxy-group in the β -position, either $\alpha\beta$ - or $\alpha\delta$ -addition takes place, and the alkyloxy-group of the resulting substance may or may not be replaced subsequently by a hydrocarbon residue. It is also shown that the influence of the β -ethoxy-group on the mode of addition is approximately the same as that of the phenyl group.

E. G.

Action of Light on Unsaturated Ketones in Presence of Uranyl Salts. PAUL PRÄTORIUS and FRANZ KORN (*Ber.*, 1910, 43, 2744—2746).—Distyryl ketone, when exposed to the action of light in presence of uranyl chloride in acetic acid suspension, yields a colourless compound, $(\text{C}_{17}\text{H}_{14}\text{O})_2$, m. p. 245° (decomp.), crystallising in needles. On oxidation with chromic acid, α -truxillic acid, benzoic acid, and carbon dioxide are formed. Accordingly, the formula



is assigned to the bimolecular compound.

A by-product is a substance soluble in acetic acid, which crystallises in colourless needles, m. p. 183° .

The red di-*p*-methoxydistyryl ketone uranyl chloride is stable towards light.

Dibenzylidenecyclopentanone uranyl chloride is decomposed to a colourless compound, crystallising in pointed prisms, m. p. 248° , which gives an orange-yellow coloration with concentrated sulphuric acid.

E. F. A.

Existence of 2:2'-Dinitrobenzoin. THOR EKECRANTZ and ALFR. AHLQVIST (*Ber.*, 1910, 43, 2606—2609. Compare Abstr., 1908, i, 347; Popovici, Abstr., 1907, i, 628).—A modification of Popovici's method (Abstr., 1908, i, 550) for the preparation of the so-called 2:2'-dinitrobenzoin is described, and the yield is increased to 0.4 gram from 25 grams of aldehyde. The product melts at 168 — 169° (corr.), not 161 — 162° , contains two atoms of hydrogen more than the benzoin, and is not oxidised to any appreciable extent by chromic acid mixture.

J. J. S.

Colour and Affinity for Mordants of Anthraquinone Derivatives. II. GUSTAV HELLER (*Ber.*, 1910, 43, 2890—2892. Compare Abstr., 1908, i, 995).—According to previous workers, the salts of anthraquinone-2:3-dicarboxylic acid, as well as those of the 1:3- and 1:4-acids, are reddish (compare Elbs and Euriich, Abstr., 1890, i, 511). Since this does not agree with the view put forward in the former paper, the author has prepared these substances, and finds that their alkaline solutions are colourless when pure. Nevertheless, they are fixed to a certain extent by some metallic hydroxides.

[With ERICH GRÜNTAL.]—*o*-Xyloyl-*o*-benzoic acid, prepared by the Friedel and Crafts' reaction according to the method previously described (Abstr., 1908, i, 994), has m. p. 167° (F. Meyer, Abstr., 1882, 848, gave 161.5°).

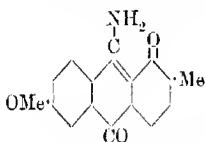
2:3-Dimethylanthraquinone has m. p. $205-206^{\circ}$ (Elbs and Eulich gave 183° ; Limpricht, Abstr., 1900, i, 599, gave 200°).

1:4-Dimethylanthraquinone has m. p. $140-141^{\circ}$ (Elbs and Eulich gave $118-119^{\circ}$).

R. V. S.

Chrysophanic Acid. OTTO A. OESTERLE and U. JOHANN (*Arch. Pharm.*, 1910, 248, 492-500).—The dimethyl ether, obtained together with a little monomethyl ether by treating chrysophanic acid with methyl sulphate, is partly demethylated by concentrated sulphuric acid on the water-bath or by aluminium chloride at 115° , yielding only one methyl ether, identical with the above. Consequently the hydroxyl groups in chrysophanic acid are not methylated with equal ease; the one which is easily methylated occupies probably a β -position, the other an α -position. Ethyl chloroacetate is a reagent which readily attacks hydroxyl groups in the α -position (D.R.P. 158277); its action on chrysophanic acid, however, does not lead to definite results; the authors claim from them, however, that one hydroxyl group is probably in a β -position.

Chrysophanic acid methyl ether and aqueous ammonia, at 140° , yield a substance, $C_{16}H_{13}O_2N, \frac{1}{2}H_2O$, m. p. $237-239^{\circ}$, which crystallises in brownish-red needles, and has the composition of an amino-chrysophanic acid methyl ether; it is converted by nitrous acid into chrysophanic acid methyl ether, a reaction which is explained, in accordance with Scholl and Parthey's results (Abstr., 1906, i, 439), by ascribing to the substance



the annexed constitution, assuming that the hydroxyl groups in chrysophanic acid are in positions 1 and 6 and the methyl group in position 2.

C. S.

So-called Methylchrysophanic Acid. OTTO A. OESTERLE and U. JOHANN (*Arch. Pharm.*, 1910, 248, 476-491).—Chrysophanic acid, when prepared from rhubarb or chrysarobin, is accompanied by a substance containing methoxyl, which is stated by Hesse to be methylchrysophanic acid (Abstr., 1900, i, 41). Gilson claims that in the case of chrysophanic acid from rhubarb the accompanying substance is rheochrysidin (*Arch. internat. Pharm. Thér.*, 1905, 14, 492). The authors show, however, that in chrysophanic acid from both sources the accompanying substance is the methyl ether of frangula-emodin. Chrysophanic acid, obtained by the oxidation of chrysarobin in alkaline solution, is methylated in the manner described previously (Abstr., 1905, i, 911), and the yellow substance, m. p. 224° , accompanying the dimethyl ether is separated therefrom by dilute alcohol; it has after repeated recrystallisation m. p. $226-227^{\circ}$ and the composition of a trimethoxymethylanthraquinone. It can be demethylated by aluminium chloride at 115° , or, better, by concentrated sulphuric acid at 160° ,

yielding a substance, m. p. 256—257°, identical with frangula-emodin (Abstr., 1908, i, 350), the identity being confirmed by a comparison of the *triacetates*, $C_{14}H_4O_3Me(OAc)_3$, yellow needles, m. p. 197—198°. Hence, the substance accompanying chrysophanic acid, obtained from chrysarobin, is a methyl ether of emodin. It can be isolated, although with considerable difficulty, by extracting the acetylated acid with alcohol at 50—55°; the acetate of emodin methyl ether thus obtained has m. p. 181—183°, but it still contains a little acetate of chrysophanic acid, because after hydrolysis, recrystallisation of the hydrolysed product, and re-acetylation, the m. p. is 190—191.5°. The hydrolysis of the acetate by aqueous potassium hydroxide yields an *emodin methyl ether*, $C_{14}H_4O_3Me(OH)_2 \cdot OMe$, orange-red needles, m. p. 206—207°, identical with that obtained by the partial demethylation of frangula-emodin trimethyl ether by aluminium chloride at 115° for three-quarters of an hour. The ether dissolves in dilute alkali hydroxides with an intense red colour, and forms a *dipropionate*, m. p. 162—164°. It is shown to be identical with Gilson's rheochrysidin by its crystallographic properties, and with Hesse's physcion (lichen-chrysophanic acid) (Abstr., 1906, i, 280) by a comparison of the *dibenzoylates*, m. p. 230°, and of the products of reduction by zinc and acetic acid. C. S.

Some Derivatives of Acenaphthenequinone. M. ZSUFFA (*Ber.*, 1910, 43, 2915—2922).—Naphthalic anhydride does not enter into the Friedel and Crafts' reaction with aromatic hydrocarbons, so that the carbonyl groups in the 1:8-position behave differently from those in the 1:2-position, as in phthalic anhydride. Acenaphthenequinone,

$(C_{10}H_6) \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix}$, however, readily undergoes this and other condensations.

With aromatic hydrocarbons or with chlorobenzene, diaryl derivatives of the type $C_{10}H_6 \begin{smallmatrix} \diagup CAr_2 \\ \diagdown CO \end{smallmatrix}$ are produced, and these are even more

readily obtained from dichloroacenaphthenone, $C_{10}H_6 \begin{smallmatrix} \diagup CCl_2 \\ \diagdown CO \end{smallmatrix}$. Acenaphthenequinone also condenses in a similar manner with dimethylaniline in the presence of zinc chloride or of concentrated hydrochloric acid, and with phenols (resorcinol) in presence of zinc chloride or tin chloride. From 9:9-diphenylacenaphthenone, diphenyl- α -naphthylmethane can be prepared with good yield, whilst from 9:9-tetramethyldiaminodiphenylacenaphthenone the corresponding hydrocarbon can also be prepared. The latter is readily oxidised to the naphthyl analogue of malachite-green.

9:9-Diphenylacenaphthenone (Beschke, Abstr., 1909, i, 918) can be obtained from acenaphthenequinone, or, better (yield almost quantitative), from dichloroacenaphthenone. In the latter case the action is vigorous, and should be moderated by the use of a solvent (carbon disulphide). When the substance is heated with alcoholic potassium hydroxide for four hours on the water-bath, 8-diphenylmethyl-1-naphthoic acid, $C_{24}H_{16}O_2$, crystallising in small, colourless laminae, m. p. 227°, is obtained. On distillation in a vacuum with two and a-half times its weight of barium hydroxide, this yields diphenyl- α -naphthylmethane,

$C_{10}H_7 \cdot CHPh_2$, which forms colourless needles, m. p. 150° . 8-Diphenylmethyl-1-naphthoic acid, when oxidised with chromic acid, gives *diphenylnaphthalide*, $C_{10}H_6 \begin{smallmatrix} \diagup CPh_2 \\ \diagdown CO \end{smallmatrix} O$, which crystallises in colourless needles, m. p. 204° .

9:9-Dichlorodiphenylacenaphthenone, $C_{24}H_{11}OCl_2$ (from dichloroacenaphthenone and chlorobenzene), forms small, colourless needles, m. p. 151° . 8-Dichlorodiphenylmethyl-1-naphthoic acid, $C_{24}H_{10}O_2Cl_2$, crystallises in small, colourless laminae, m. p. $224-225^\circ$.

9:9-Tetramethyldiaminodiphenylacenaphthenone, $C_{28}H_{28}ON_2$, is prepared by heating acenaphthenequinone with dimethylaniline and a small quantity of concentrated hydrochloric acid to 150° for three hours. It forms small, yellow laminae or needles, m. p. $204-205^\circ$. Its solution in glacial acetic acid is coloured malachite-green by oxidising agents, but the coloration disappears on dilution with water. Prolonged boiling with alcoholic potassium hydroxide leaves the compound unaffected. The hydrochloride, $C_{28}H_{28}ON_2 \cdot 2HCl$, prepared with hydrogen chloride in benzene solution, forms colourless needles, which with water regenerate the base. The picrate,

$C_{28}H_{28}ON_2 \cdot 2C_6H_3O_7N_3$, forms lemon-yellow crystals. The dimethiodide, $C_{28}H_{28}ON_2 \cdot 2MeI$, has m. p. $224-225^\circ$ (decomp.). When 9:9-tetramethyldiaminodiphenylacenaphthenone is boiled for four hours with amyl-alcoholic potassium hydroxide, 8-tetramethyldiaminodiphenylmethyl-1-naphthoic acid, $C_{28}H_{28}O_2N_2$, is obtained. It crystallises in pale yellow needles, m. p. $260-262^\circ$, and is soluble in acids and alkalis. The barium salt is sparingly soluble in water. Distillation of the acid with barium hydroxide yields tetramethyldiaminodiphenyl- α -naphthylmethane, $C_{10}H_7 \cdot CH(C_6H_4 \cdot NMe_2)_2$, which forms yellow needles, m. p. $161-162^\circ$, and on oxidation gives naphthyl-malachite-green.

Anhydrosorcinolacenaphthenone, $C_{10}H_6 \begin{smallmatrix} \diagup C \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} C_6H_3 \cdot OH \\ C_6H_3 \cdot OH \end{smallmatrix} O$, is prepared by heating acenaphthenequinone with resorcinol and zinc chloride for two hours at 180° . It is a pale brown, amorphous powder, which is soluble in alkali hydroxides, giving a yellowish-red coloration and a green fluorescence. R. V. S.

Derivatives of the Dextro-Antipode of Natural l-Menthol. LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 714-718. Compare Skwortzoff, *ibid.*, 1910, 42, 55).—The oil of Bucco leaves, freed from diosphenol by repeated treatment with 20% alkali hydroxide, was dried and fractionated. The fraction boiling at $190-225^\circ$ was reduced with sodium and alcohol, the product distilled in steam, and the distillate then extracted with ether, dried, and redistilled. The fraction boiling at $200-220^\circ$, containing most of the menthol, was then converted into sodium methylxanthate, which, by the action of iodine, was converted to the disulphide, thus:

$C_{15}H_{19}O \cdot CS_2Na + 2I = S_2(CS \cdot O \cdot C_{15}H_{19})_2 + 2NaI$,
m. p. $92-92.5^\circ$, $[a]_D + 183.4^\circ$, $[a]_D + 226.3^\circ$.

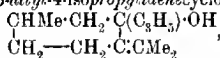
The latter with potassium cyanide gave the anhydride, $(C_{15}H_{19}O \cdot CS)_2S$, m. p. $147.5-148^\circ$, forming yellowish-green, hexagonal crystals.

In toluene solution at 20° it gave $[\alpha]_D +46.42^\circ$, $+46.50^\circ$, $[\alpha]_x +21.17^\circ$, the corresponding *l*-menthylxanthic anhydride giving $[\alpha]_D -46.50^\circ$, $[\alpha]_x -21.30^\circ$. The new compound must therefore be a derivative of *d*-menthol, and the two substances are optical antipodes. The disulphide of *l*-menthol has $[\alpha]_D -182.8^\circ$, $[\alpha]_x -225.1^\circ$. By saponification the *d*-menthylxanthic anhydride yields a menthol, m. p. 42°. Z. K.

Constitution of Fenchone. V. and VI. LOUIS BOUYEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 963—968, 968—973).—These two papers are in continuation of work published previously (this vol., i, 686), and record results given already in part (*Abstr.*, 1909, i, 497, 595). Fuller experimental details and an outline of the principles underlying the syntheses effected are now given.

The following results are new. *apofenchene* hydrochloride (*Abstr.*, 1908, i, 193), treated in succession with magnesium ethyl bromide and carbon dioxide, furnishes an acid having the same boiling point as dihydrofencholenic acid, but yielding an anhydride having b. p. 92.2/20 mm., which is 3° lower than that of the expected anhydride (this vol., i, 573), and an amide, having m. p. 104°, as against 108° for dihydrofencholenamide, although it forms nacreous leaflets in all respects similar to those formed by the latter. T. A. H.

Action of Magnesium on a Mixture of Allyl Bromide and Pulegone (Synthesis of 1-Methyl-3-allyl-4-isopropylidenecyclohexan-3-ol). G. G. von FERSEN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 681—683).—1-Methyl-3-allyl-4-isopropylidenecyclohexan-3-ol,

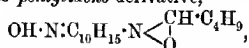


obtained when magnesium is treated with a small quantity of allyl bromide and a mixture of pulgone and allyl bromide then added drop by drop, has b. p. 135—135.5°/27 mm., $D_4^{25} 0.9264$, $n_D^{20} 1.49039$; it is a colourless liquid with a pleasant odour, which on oxidation with permanganate yields a complex mixture of acid and neutral products. Z. K.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. II. α -Pinene-*o*-hydroxylamineoxime. GUIDO CUSMANO (*Gazzetta*, 1910, 40, ii, 122—131. Compare this vol., i, 685).—From α -pinene bisnitrosochloride, the author has prepared α -pinene-*o*-hydroxylamineoxime similarly to the *d*-limonene-*o*-hydroxylamineoxime previously described (*loc. cit.*), but he has found that the compound reacts like the ordinary *m*-hydroxylamineoximes, so that the anomalous behaviour of the *d*-limonene derivative still requires explanation.

α -Pinene-*o*-hydroxylamineoxime forms lustrous needles, which decompose about 140°. It reduces Fehling's solution in the cold, and is soluble in alkalis, whilst with acids it yields monobasic salts. The hydrochloride, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2 \cdot \text{HCl}$, which is formed in addition to the free base in the preparation of the substance, crystallises in tufts of silky needles, m. p. about 170°; when the solvent contains water, it

crystallises in hexagonal laminae with H_2O , and these sinter at about 100° , decomposing at 165° . The *sulphate*, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2\cdot\text{H}_2\text{SO}_4$, forms four-sided tablets. By the action of nitrous acid on either of these salts, the *isonitroamineoxime* is formed (compare this vol., i, 574). The hydroxylamine group of the hydroxylamineoxime reacts with aldehydes. The *pentylidene* derivative,



forms flat, quadrangular crystals, m. p. 150° . The *benzylidene* derivative, $\text{OH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_{15}\cdot\text{N}\begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, crystallises in hexagonal laminae, m. p. 167° . The *p-nitrobenzylidene* compound, $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}_2\cdot\text{C}_6\text{H}_5\text{O}$, forms yellow crystals, m. p. $163\text{--}165^\circ$.

Pinene-*o*-hydroxylamineoxime is decomposed by very dilute oxalic acid, with formation of carboxime and hydroxydihydrocarboxime, so that instead of the elimination of the oxamic grouping, the destruction of the piceanic ring is effected. These two substances are formed in all the reactions in which the hydroxylamineoxime reacts in an acid medium, and hence they occur as by-products in its preparation. By the action of alkalis, the hydroxylamineoxime in time loses the oxamic group, hydroxylamine and nitrosopinene being formed.

o-Nitrosoisnitrosopinene, $\text{C}_{10}\text{H}_{15}\begin{array}{c} \text{NO} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{OH} \end{array}$, may be obtained by oxidis-

ing α -pinene-*o*-hydroxylamineoxime, preferably by dissolving it in dilute sulphuric acid and adding the calculated quantity of potassium dichromate, the dilute solutions being kept cool with ice. It is a crystalline substance, which explodes at about 60° , and readily oxidises in the air, absorbing one atom of oxygen, with production of a yellow substance. When a solution of the hydroxylamineoxime hydrochloride is treated with iron alum, a substance is obtained containing 51% of iron; it is orange-yellow in colour, and decomposes at $110\text{--}120^\circ$.

R. V. S.

[Essential Oils.] HEINRICH HAENSEL (*Berichte von H. Haensel*, April to September 1910, 6—53).—The flowers of *Gnaphalium avicularium*, used as an insectifuge, yielded 0.04% of dirty green, aromatic oil, which solidified at 4° and had D_{20}^{20} 0.921. After treatment with animal charcoal, it was bluish-green in colour, solidified at 7° , had acid number 14.45, ester number 9, and was incompletely soluble in 95% alcohol. The insoluble matter consisted of stearopten, m. p. $48\text{--}50^\circ$, containing a bluish-green colouring matter. The soluble portion of the oil contained (1) an *acid*, m. p. $34\text{--}36^\circ$, with an odour recalling that of hexoic acid, (2) *p*-cresol, and (3) an alcohol having a fruity odour.

Syrian peppermint oil (compare this vol., i, 401) gave a terpeneless fraction having the following constants: acid number 1.87, ester number 22.4, acetyl ester number 180 (one hour), corresponding with 6.24% ester menthol and 51.73% free menthol. The crude oil yielded 5% of terpene, having D_{20}^{20} 0.8880.

Datura Stramonium leaves yielded 0.045% of a volatile oil of dark brown colour and tobacco-like odour. It had D_{20}^{20} 0.9440, solidified at 20° , and after treatment with animal charcoal showed acid number

52.4, and ester number 9.57. The saponified oil contained a minute quantity of an alcohol having a strong odour of tobacco. The aqueous distillate was alkaline and of blue colour, but became colourless on addition of acid, regaining the blue colour on addition of alkali.

Dalmatian yellow sunflowers (*Sonnengoldblumen*) furnished 0.235% of oil, D_{20}^{25} 0.9100, n_D^{20} 1.4510, of greenish-yellow colour and pleasant, sweet aroma. It had acid number 8.9 and ester number 87.66, corresponding with 24.12% of alcohol, $C_{16}H_{18}O$. T. A. H.

Spearmint Oil. F. ELZE (*Chem. Zeit.*, 1910, 34, 1175).—The carvone-free residue of spearmint oil has an intense spearmint odour, and on distillation under reduced pressure gives the following fractions: b. p. 40–45°/4 mm., 15%, containing 2.8% esters; b. p. 45–75°/4 mm., 15%; b. p. 75–80°/4 mm., 24%, containing 19% esters; b. p. 80–85°/4 mm., 7.5%; and 85–100°/4 mm., 35.0%, containing 31% esters. From the first of these fractions phellandrene was isolated. The last fraction, freed from aldehydes and phenols, furnished on hydrolysis acetic and valeric acids and dihydrocuminyl alcohol. Dihydrocuminyl acetate has the characteristic odour of spearmint oil. T. A. H.

Cold Vulcanisation of Caoutchouc. B. B. BYSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 638–647).—A criticism of Weber's theory of the vulcanisation of caoutchouc with sulphur chloride, S_2Cl_2 . The chemical explanation of the process is not satisfactory. Regarding caoutchouc as a heterogeneous disperse system consisting of two liquid phases, it will probably have the general properties of a colloid, such, for instance, as the property of adsorption. The change in caoutchouc on vulcanisation with sulphur chloride is due to the adsorption of the latter, the process of vulcanisation is thus physical not chemical. The connexion between the amount of sulphur contained in the caoutchouc after vulcanisation and the concentration of the benzene solutions of sulphur chloride employed has been studied, and the resulting curve, which is hyperbolic, is drawn. Z. K.

Chlorophyll Group. VIII. Formation of Phyllotaonin from Chlorophyllan. HENRY K. MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1910, 28, 48–52. Compare this vol., i, 692).—When chlorophyllan (15 grams), obtained from stinging nettles, is left for twenty-four hours with 200 c.c. of methyl-alcoholic potassium hydroxide solution, hydrolysis takes place. The mass is poured into 2 litres of water, and the phytol removed by extraction with ether; acetic acid is added, and the ether extraction repeated. The ethereal solution is fractionated by extracting with gradually increasing amounts of hydrochloric acid, namely, from 1 to 20%. The product, soluble in 1% hydrochloric acid, contains chlorophyllanic acid, and the solution in 18% hydrochloric acid gives all the characteristic absorption bands of allophyllotaonin (Kózniewski and Marchlewski, *Abstr.*, 1907, i, 867), and when treated with alkalis gives the absorption bands of phyllotaonin. J. J. S.

Commercial Azolitmin. PAUL SCHEITZ (*Zeit. anal. Chem.*, 1910, 49, 735–736. Compare following abstract).—Azolitmin occurs in commerce in the form of bluish-black scales, contains very little

mineral matter, dissolves in water with a red coloration, but becomes insoluble in water after heating at 100° during three to four hours. It dissolves in ammonia or alkali solutions, forming blue liquids, but is not re-precipitated therefrom by acids, the solutions merely changing colour to red. The substance appears to be an ammonium salt, since it evolves about 8.5% of ammonia on treatment with alkalis.

By dissolving commercial azolitmin in ammonia solution, recovering the colouring matter by adding excess of hydrochloric acid and warming, and then purifying the precipitated product by boiling with alcohol, about 22% of a nitrogenous substance closely resembling the azolitmin of litmus is obtained. This is greenish-black in colour, and almost insoluble in water, alcohol, or acetone; it absorbs ammonia gas, forming a bluish-black product, which dissolves in water, forming a red solution from which the purified azolitmin is regenerated on addition of excess of acid or salts of heavy metals. This ammonium compound is a useful indicator. Similar products are obtained with methylamine and dimethylamine.

T. A. H.

The Portion of Litmus Soluble in Alcohol. PAUL SCHRETZ (*Zeit. anal. Chem.*, 1910, 49, 736—739. Compare preceding abstract).

—The isolation of a blue colouring matter distinct from azolitmin and soluble in alcohol is described. When crude litmus is treated with dilute hydrochloric acid until no more carbon dioxide is evolved, the red solution formed slowly deposits, when warmed at 100°, a dark brown precipitate, which, when boiled with water, separates into (a) a finely-divided reddish powder, containing some azolitmin, but consisting chiefly of products soluble in alcohol, and (b) a grey-steel product, mainly composed of azolitmin, but containing a little alcohol-soluble matter.

When boiled with a mixture of alcohol (2 parts) and water (1 part), preparations a and b furnish (1) azolitmin, insoluble in aqueous alcohol, and (2) a mixture of Kane's erythrolein and erythrolitmin with a third substance, which is bright brown in colour, all of these being soluble in hot aqueous alcohol. Of these three substances the first two can be eliminated by extraction with hot acetone, leaving the third in an impure form, from which a purer form can be prepared by dissolving it in hot aqueous alcohol, filtering, and cooling, when it is deposited as bright brown powder, equivalent in weight to 1.5% of the purified litmus. This is soluble in formic acid, pyridine, or ammonia, forming a bluish-violet solution with the last-mentioned solvent. It absorbs ammonia gas, becoming hot, and forming a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin (compare preceding abstract). Similar substances are formed by absorption of methylamine and dimethylamine. T. A. H.

Phycocerythrin and Phycocyanin from *Ceramium rubrum* (Huds.). HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1910, 69, 169—239. Compare Hanson, *Proc.*, 1909, 25, 117; Molisch, *Abstr.*, 1895, i, 556; 1906, ii, 118; Gaidukov, *ibid.*, 1904, i, 439).—Details are given for the preparation of solutions of pure phycocerythrin and phycocyanin from *Ceramium rubrum*. The isolation is based on the

fact that both colouring matters can be obtained in a crystalline form by the addition of the requisite amount of ammonium sulphate to their solutions; the phycoerythrin is deposited when 18 grams of sulphate, and the phycocyanin when 25 grams of sulphate, have been added to 100 c.c. of the solution. Magnesium sulphate may also be used, but larger quantities are necessary. Phycocyanin can be precipitated in an amorphous state by completely saturating its solution with sodium chloride, but phycoerythrin is not precipitated under these conditions.

The phycoerythrin solution has a carmin-red colour, and when dilute a tinge of violet; concentrated solutions have an orange colour, and all solutions give a characteristic orange-yellow fluorescence. It gives all the characteristic reactions of a protein, including the biuret reaction (compare Hanson). The colouring matter dissolves in water containing a small amount of alkali or of neutral salts, but is deposited in a crystalline form when all salts are removed by dialysis. It is insoluble in ordinary organic solvents, but dissolves in dilute acetic acid and also in extremely dilute hydrochloric acid, yielding solutions which do not fluoresce.

The conclusion is drawn that the acid decomposes the phycoerythrin into protein and colouring matter, and that the precipitate obtained on adding a small amount of sodium carbonate to the acid solution is the colour-constituent. The addition of a trace of acid to the ordinary solution precipitates the phycoerythrin.

The small amounts of salts which are necessary to keep the colouring matter in solution are sufficient to cause complete precipitation when the solution is heated at 90° . The addition of traces of acid reduce the temperature of coagulation, and the amount of acetic acid necessary to give the ordinary protein reaction produces coagulation at $53-55^{\circ}$. The addition of a trace of alkali prevents coagulation.

The action of pepsin and trypsin is represented as first causing a decomposition of the phycoerythrin into protein and colour-constituents, and then the decomposition of the protein. After the digestion with pepsin, the colour-constituent can be removed by shaking with amyl alcohol. The results of analyses of phycoerythrin gave: C=50.82, H=7.01, N=15.37, S=1.60, and O=25.20%.

The absorption spectrum of pure phycoerythrin contains three characteristic bands, two between *D* and *E*, and one between *E* and *F*. These bands have their maxima at $\lambda=569-565$, $541-537$, and $498-492 \mu\mu$. On dilution the second band disappears before the third.

Phycocyanin crystallises in rhombic plates, quite different from the crystals described by Molisch. It gives the protein reactions; its solubility in water, saline solutions, and dilute alkalis is similar to that to phycoerythrin, as is also its behaviour towards acids, pepsin, and trypsin.

A solution of phycocyanin containing the smallest possible amount of salt is completely coagulated when heated at 82° , and the addition of a little acetic acid reduces this to $46-48^{\circ}$.

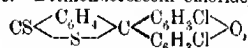
The solutions of phycocyanin exhibit two absorption bands, one between *C* and *D* and the other between *D* and *E*, the maxima being at λ 618-613 and 553-549 $\mu\mu$.

J. J. S.

Sulphur Dyes. II. HERMANN WICHELHAUS (*Ber.*, 1910, 43, 2922—2926. Compare Abstr., 1907, i, 232; Erdmann and Schäfer, this vol., i, 718).—The distillate from 20 kilograms of cellulose (cotton) consisted of 5.7 litres of an aqueous liquid and 1 litre of an oily mass. From both of these only one phenol could be isolated, namely, phenol itself. The author has put forward the view that a sulphur dye could be formed from phenol, thus explaining the origin of sulphur dyes from cellulose. As an intermediate product, phenoxiquinone claims attention. Molecular-weight determinations in the case of the analogous toluquinone and thiotoluquinone confirm the original statement (*Ber.*, 1872, 5, 248) that phenoxiquinone has the formula $C_{18}H_{14}O_4$. When it is boiled with alkali sulphides and sulphur, or, better, heated with those substances under pressure at 200—220°, a sulphur dye is formed, which, after purification, contains C 75%, H 5%, S 12%. It is a dark brown powder, insoluble in alkaline carbonates, ammonia, and acids, but soluble in alkali sulphides. The last-named solution dyes cotton dark brown.

Phenoxiquinone also yields a dye free from sulphur when it is kept for ten days at the ordinary temperature in contact with sodium acetate and water. The crude product is purified by solution in sodium hydroxide, re-precipitation with acid, removal of phenol by means of steam, and final precipitation as iron salt, which is decomposed by hot hydrochloric acid. So obtained, the acid has m. p. 110°. When dissolved in sodium carbonate, it dyes cotton brown.

Fluorescein yields sulphur dyes when heated with sulphur or sulphur and sodium sulphide, but it is not possible to obtain them in a pure state. Dithiofluorescein chloride,

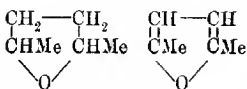


which is not a dye, condenses in presence of sulphuric acid or anhydride to form sulphur derivatives which are dyes. R. V. S.

Velocity of the Transformation of Oxonium Bases, Colour Bases, and Cyanides into Carbinol Bases and Leucocyanides. WOLF. J. MÜLLER (*Ber.*, 1910, 43, 2609—2613. Compare this vol., i, 407; Gerlinger, Abstr., 1904, i, 1040).—The velocity constants of various reactions studied by Hantzsch and his pupils (Abstr., 1900, i, 113, 256) have been recalculated from Hantzsch's data, and it is shown that, using the equation for a bimolecular reaction, quite concordant values for K are obtained.

Hantzsch's statement to the contrary is due to mistakes in calculation. J. J. S.

Stereochemistry of 1:4-Dimethyltetrahydrofuran and 1:4-Dimethylfuran. ANGEL DEL CAMPO Y CERDÁN (*Anal. Fis. Quim.*, 1910, 8, 227—244).—A geometrical study of the causes of the difference of stability of the two compounds (annexed formulae) from the point of view of the "tension" theory. It is shown that the mass of



the groups in the first compound causes a greater strain or deforma-

tion from the simple regular tetrahedral form, representing a carbon atom combined with four hydrogen atoms, than those of the second; the latter is therefore the more stable substance, as is actually the case.

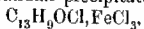
W. A. D.

ω-Hydroxy-*s*-methylfurfuraldehyde. HENRY J. H. FENTON (*Ber.*, 1910, 43, 2795—2796. Compare Fenton and Gostling, *Trans.*, 1899, 75, 430; Fenton and Robinson, *ibid.*, 1909, 95, 1338; Alberda van Ekenstein and Blanksma; Erdmann, this vol., i, 762).—Attention is drawn to the fact that the hydroxyfurfuraldehydes prepared from the *ω*-bromomethylfurfuraldehyde and from inulin by the action of oxalic acid are identical. They yield the same phenylhydrazones and the same oxidation product, and both are to be regarded as *ω*-hydroxy-*s*-methylfurfuraldehyde.

J. J. S.

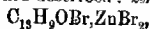
Triphenylmethyl. XIX. Quinocarbonium Salts. MOSES GOMBERG and LEE H. CONE (*Annalen*, 1910, 376, 183—238. Compare *Abstr.*, 1907, i, 504; 1909, i, 144; this vol., i, 55).—Not merely salts of triphenylmethane and xanthenol, but also those derived from diphenoxanthhydrol, dinaphthaxanthhydrol, thioxanthenol, and bromothioxanthenol exist in colourless benzenoid and yellow quinonoid forms. The acridol salts are also regarded as quinocarbonium salts. Diphenoxanthhydrol exists in the solid form as the colourless benzenoid carbinyl chloride, and appears to be incapable of yielding a stable coloured chloride hydrochloride; it can, however, be readily transformed by means of sulphur dioxide, sulphuric acid, or metallic halides. Dinaphthaxanthhydrol, on the other hand, yields a perfectly stable and intensely coloured chloride dichloride in addition to the colourless carbinol chloride.

Xanthhydryl chloride, $O \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CHCl}$ (compare Werner, *Abstr.*, 1902, i, 50), can be prepared by the action of hydrogen chloride on xanthhydrol in absolute ethereal solution. It is extremely sensitive to traces of moisture, but can be obtained in colourless needles, m. p. 73—75° after sintering at 71°. When further heated, hydrogen chloride is evolved, and at 170—175° the evolution is rapid. Hydrogen chloride is also evolved when the salt is heated with xylene or nitrobenzene, but whether dioxanthylene is formed or not has not been determined. It does not yield a stable quinonoid hydrochloride, but the following double salts have been prepared: *zincichloride*, $C_{13}H_9OCl_2ZnCl_2$, yellow, granular precipitate; *ferrichloride*,



m. p. 193° (compare Werner); *periodide*, $C_{13}H_9OCl_2I_3$, prepared from benzene solutions, dark blue crystals, m. p. 90°.

Xanthhydryl bromide, $O(C_6H_4)_2CHBr$, is much more stable than the chloride, and crystallises from light petroleum solutions in long, colourless needles, m. p. 88—90°, which turn yellow when kept. The pure quinocarbonium salt has not been obtained, but the following double salts are described: *zincibromide*,

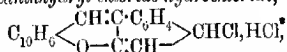


slender, orange-yellow crystals; *periodide*, dark blue crystals with four or six atoms of iodine.

Xanthhydryl perchlorate, $C_{13}H_9O \cdot ClO_4$, forms dark red crystals, m. p. 208—209°.

Dinaphthaxanthen is best prepared by heating pure *p*-dihydroxynaphthylmethane (Manasse, Abstr., 1894, i, 577) with glacial acetic acid in a current of hydrogen chloride. Dinaphthaxanthhydryl can be prepared by Fosse's methods (Abstr., 1902, i, 171).

Dinaphthaquinoxanthhydryl chloride hydrochloride,

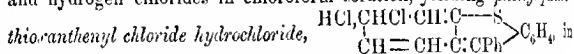


prepared by the action of acetyl chloride and hydrogen chloride on a benzene solution of the hydrol or on the anhydride in chloroform solution, crystallises in dark red needles, m. p. 228—229° (decomp.) and is extremely stable. When a current of air is passed through its toluene solution at 100°, hydrogen chloride is evolved, and *dinaphtha-*

xanthhydryl chloride, $O \begin{array}{c} C_{10}H_6 \\ C_{10}H_6 \end{array} \begin{array}{c} \text{CHCl} \\ \text{CHCl} \end{array}$, is precipitated on the

addition of light petroleum to the concentrated solution as slender, colourless needles, m. p. 205—206°, which are comparatively stable. The *zincchloride*, $C_{21}H_{13}OCl \cdot ZnCl_2$, forms a stable, orange-red, crystalline mass, and the *periodide*, $C_{21}H_{13}OCl \cdot I_2$, is precipitated when iodine is added to a benzene solution of the chloride. *Dinaphthaquinoxanthhydryl bromide hydrobromide*, $C_{21}H_{13}OBr \cdot HBr$, forms a red, crystalline mass, and is even more stable than the hydrochloride. The *perchlorate*, $C_{21}H_{13}O \cdot ClO_4$, forms red crystals with a golden reflex, is not molten at 260°, and is only slowly decomposed by water. Dinaphthaxanthen reacts with a carbon disulphide solution of bromine, yielding a red *dinaphthaxanthhydryl bromide perbromide* according to the equation: $O : (C_{10}H_6)_2 : CH_2 + 2Br_2 = O : (C_{10}H_6)_2 : CHBr \cdot Br_2 + HBr$, even when less than the theoretical amount of bromine is used. Chlorine reacts with a carbon tetrachloride solution of the xanthen, yielding an insoluble chloride perchloride.

Phenylthioxanthenol, prepared by a modification of Bünzly and Decker's method (Abstr., 1904, i, 912), reacts with a mixture of acetyl and hydrogen chlorides in chloroform solution, yielding *phenylquinoxanthioanthenyl chloride hydrochloride*,

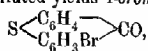


the form of dark red crystals, the colour of which is much deeper than that of the corresponding oxygen compound. When dry air is led through a benzene solution of the red compound, hydrogen chloride is evolved and *phenylthioxanthenyl chloride*, $S \begin{array}{c} C_6H_4 \\ C_6H_4 \end{array} \begin{array}{c} S \\ S \end{array} PhCl$, is

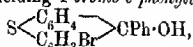
formed. This crystallises from light petroleum in colourless prisms, m. p. 114—115°, after sintering at 110°, and turns red on exposure to the air. The chloride reacts with "molecular" silver in the presence of dry benzene, yielding a brownish-red, unsaturated compound, which is stable in the absence of air, but combines readily with oxygen, yielding the *peroxide*, $S : (C_6H_4)_2 : CPh \cdot O \cdot O \cdot CPh : (C_6H_4)_2 : S$.

which crystallises in colourless, hexagonal prisms, m. p. 187—188°, after sintering at 175—180°.

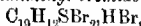
The 2-phenylthiol-4-bromobenzoic acid, $C_{13}H_9O_2SBr$, prepared by Goldberg's method (Abstr., 1905, i, 59), crystallises from glacial acetic acid, has m. p. 230—231°, and when warmed with concentrated sulphuric acid and then diluted yields 4-bromothioxanthone,



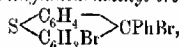
as slender, yellow needles, m. p. 165°, which reacts with phenyl magnesium bromide, yielding 4-bromo-9-phenylthioxanthanol,



as an oil, from which a few crystals, m. p. 75—80°, can be obtained. 4-Bromo-9-phenylquinothioxanthanyl bromide hydrobromide,

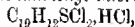


forms dark red needles, which are immediately decomposed by moisture. 4-Bromo-9-phenylthioxanthanyl bromide,



is usually slightly coloured, has m. p. 159°, after sintering at 150°, and after treatment with silver it does not yield a peroxide. In this respect it resembles the monohalogenated triphenylmethyl halides, as also in the readiness with which the two atoms of bromine are replaced by chlorine when the bromide is shaken with benzene and silver chloride.

4-Chloro-9-phenylquinothioxanthanyl chloride hydrochloride,



obtained by shaking the corresponding tribromo-derivative with benzene and silver chloride, or by saturating the benzene solution with hydrogen chloride, is somewhat paler in colour than the bromide, and gives up hydrogen chloride when dry air is passed through its benzene solution at the ordinary temperature. The product, 4-chloro-9-phenylthioxanthanyl chloride, $C_{19}H_{12}SCl_2$, is readily soluble in all solvents, and has not been obtained pure. 9-Phenylthioxanthanyl perchlorate, $C_{19}H_{11}S \cdot ClO_4$, crystallises in slender, dark red plates, m. p. 195—210°, after sintering at 150°, and thioxanthone perchlorate, $C_{13}H_9OS \cdot ClO_4$, in transparent, brown prisms.

A number of compounds of dimethylpyrone, benzo-γ-pyrone, anthone, aldehydes, ketones, and phenols with acids have been prepared. Many of them have been described previously (compare Collie and Tickle, Trans., 1899, 75, 710; Feist, Abstr., 1892, 811; Meyer and Villiger, Abstr., 1901, i, 658; Vorländer, Abstr., 1903, , 493; Werner, Abstr., 1902, i, 686; Ruhemann, Trans., 1900, 77, 85, 1123), but the following are new. Dimethylpyrone derivatives: $C_7H_4O_2 \cdot ZnCl_2$, colourless crystals, m. p. 200°; zincchloride, $C_7H_4O_2 \cdot HCl \cdot ZnCl_2$, colourless, hygroscopic crystals; $C_7H_4O_2 \cdot H_2Cl_2$, colourless crystals, m. p. 149°; mercuric chloride, $C_7H_4O_2 \cdot HCl \cdot HgCl_2$; irridchloride, $3C_7H_4O_2 \cdot 2FeCl_3$, lemon-yellow crystals, m. p. 173—174°; hydrobromide, $C_7H_4O_2 \cdot HBr$, m. p. 194—196°, after sintering at 188°; $C_7H_4O_2 \cdot ZnBr_2$, colourless crystals, m. p. 204—205°. Derivatives of

benzo- γ -pyrone: *hydrochloride*, $C_9H_6O_2.HCl$, m. p. $101-102^\circ$ (decomp); $C_9H_6O_2.ZnCl_2$, colourless crystals, m. p. $250-251^\circ$, after sintering at 205° ; *zincchloride*, $(C_9H_6O_2.HCl)_3.ZnCl_2$; $C_9H_6O_2.HgCl_2$, colourless crystals; *hydrobromide*, $C_9H_6O_2.HBr$, m. p. 175° , after sintering at 169° ; *hydrobromide periodide*, dark blue crystals.

The hydrochloride and hydrobromide of dimethylpyrone are decomposed when heated with benzene and a current of dry air drawn through the solution, and the salts of benzo- γ -pyrone are even less stable. Dimethylpyrone does not appear to react with phenyl magnesium bromide.

Although Perkin (Trans., 1896, 69, 1439) states that xanthone does not combine with acids, the following compounds have been prepared: *xanthone hydrochloride periodide*, prepared by passing hydrogen chloride into a carbon disulphide solution of xanthone and iodine; *xanthone hydrobromide*, $C_{13}H_8O_2.Br$, is unstable and forms pale yellow crystals; the *perbromide*, $C_{13}H_8O_2.HBr.Br_2$, forms orange-coloured crystals and gives up bromine readily; β -*phenonaphthaxanthone hydrobromide*, $C_{17}H_{10}O_2.HBr$, forms yellow needles; 5-methoxyxanthone *hydrobromide*, $C_{14}H_{10}O_3.HBr$, pale yellow crystals, and *xanthone stannichloride*, $(C_{13}H_8O_2)_2.SnCl_4$, pale yellow crystals, m. p. 245° .

These compounds are compared with the additive compounds formed by the union of carbonyl derivatives with acids and salts. In the latter group of additive compounds the acid, for example, hydrogen chloride, is, almost undoubtedly, added on to the carbonyl group, and it is suggested that probably the same type of reaction takes place with dimethylpyrone, xanthone, etc. The products are probably not salts, and their decomposition into oxygen compound plus acid is probably not a process of hydrolysis, but of dissociation (addenda-dissociation of Vorländer).

Fluorenone hydrobromide periodide, $C_{13}H_8O_2.HBr.I_2$, forms coloured crystals; *phenanthraquinone hydrobromide*, $C_{14}H_8O_2.HBr$, is unstable, and anthraquinone does not appear to yield a hydrobromide. Anisaldehyde hydrobromide (compare Vorländer) is stable, and can be prepared at the ordinary temperature. *p*-Hydroxybenzaldehyde, resorcyaldehyde, piperonal, vanillin, and β -naphtholaldehyde all yield comparative stable, yellow *hydrobromides*.

Phenols which can react in the tautomeric ketonic forms can also form hydrobromides, for example, orcinol, phloroglucinol, and quinol, whereas resorcinol, pyrogallol, guaiacol, and the methyl ethers of resorcinol, quinol, and pyrogallol do not combine with hydrogen bromide.

The application of the quinocarbonium theory to the cases of *pararos*aniline, phenylated rosanilines, amino-azines, aurin, phenolphthalein, fluorescein, and fluorone is discussed. The theory accounts for the fact that phenolphthalein is incapable of yielding a coloured hydrobromide, that fluorescein yields a mono-hydrobromide (Hewitt and Tervet, Trans., 1902, 81, 663), and dimethylfluoran a *dihydrobromide*, $C_{10}H_{10}O_2.2HBr$, slender, orange-yellow crystals. J. J. S.

Brominated and Iodinated Products of Curare Alkaloids
JÓZEF BURACZEWSKI and Z. ZBIEŃSKI (Bull. Acad. Sci. Cracov, 1910,
359-354) and two alkaloids, curine and tubocurarine, in commer-

cial tubocurare from the bamboo have been examined with regard to their behaviour towards bromine and iodine. Curine, in ethereal solution, gives with bromine a straw-yellow precipitate, probably of a dibromo-derivative, but does not yield a precipitate with iodine. An alcoholic solution, however, by treatment with iodine in carbon disulphide gives a brownish-red precipitate, which dissolves very easily in alkalis or in aqueous ammonia, being re-precipitated by acids in the form of an almost black substance containing 49.65% of iodine. Curine, therefore, resembles strychnine in its behaviour towards bromine, but not towards iodine. An alcoholic solution of tubocurarine and iodine in carbon disulphide give a similar precipitate of like properties. The formation of these iodinated products is of use in the examination of crude tubocurare, because the colour reactions of curine and tubocurarine are applicable only to the isolated alkaloids, not to crude tubocurare. C. S.

Action of Chlorine on Strychnine, Brucine, Cinchonine, Quinine, and Other Alkaloids. JÓZEF BURACZEWSKI and Z. ZATKIEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 355—362).—On account of the oxidising action of chlorine, chlorinated derivatives of the alkaloids are more difficult to prepare than brominated or iodinated derivatives. By passing a slow current of dry chlorine over the well-cooled and shaken dry alkaloids, the authors find that chlorinated products are obtained containing usually more halogen than is the case in the usual methods of chlorination; heat is developed and frequently hydrogen chloride given off, although sometimes only after some time. By this process, strychnine absorbs five atoms of chlorine, brucine three, cinchonine four, cinchonidine three, quinine six, quinidine six, thebaine four, and morphine one. In these chlorinated alkaloids at least a part of the halogen is bound in the same way as the halogen in the brominated or iodinated derivatives, because all of the products except the chlorinated morphine yield with warm water an insoluble precipitate and a soluble salt of a chlorinated base. C. S.

Action of Acetone on Di-iodostychnine and on the Brominated Products of Strychnine and of Some Other Alkaloids. JÓZEF BURACZEWSKI and MIECISŁAS DZIURZYŃSKI (*Bull. Acad. Sci. Cracow*, 1910, 363—366).—Complicated reactions take place during the prolonged boiling necessary for the solution of di-iodostychnine (*Abstr.*, 1908, i, 1007) in acetone. Two colourless, non-poisonous, crystalline products are obtained, which do not exhibit the properties of strychnine or of its salts. Strychnine hydriodide and iodide, $C_{22}H_{22}O_2N_2I_2.HI$, are also produced, together with iodoacetone. Dibromostychnine and tetrabromostychnine (and also pentabromoquinine) likewise cause the formation of bromoacetone when they are boiled with acetone. The formation of these halogenated acetones is regarded as evidence that the method of union of the two iodine atoms in di-iodostychnine is the same as that of two bromine atoms in dibromo- or in tetrabromo-strychnine. C. S.

Oxidation Products of Brominated Strychnines. I. JOZEF BURACZEWSKI and T. NOWOSIELSKI (*Bull. Acad. Sci. Cracow*, 1910, 154—162).—On account of the scarcity of characteristic oxidation products of strychnine and of their importance for the determination of its constitution, the authors have commenced a more thorough examination of the precipitates obtained by Buraczewski and Dziurzyński (*Abstr.*, 1909, i, 672). These authors found that by warming dibromostrychnine with water a precipitate is formed; the bromostrychnine obtained from the filtrate yielded by bromination a mixture of tri- and tetra-bromostrychnines, which likewise yielded a precipitate when warmed with water. The basic substance obtained from the aqueous filtrate in the latter case has been brominated, yielding a product which again gives a precipitate when warmed with water. The first-mentioned precipitate dissolves almost completely in alcohol, but the others are separated by this solvent into a soluble and an insoluble portion. The insoluble portions behave alike towards alkalis, acids, and solvents, and are recrystallised, after being mixed, from hot acetic acid by the addition of water, yielding a substance, $C_{21}H_{20}O_4N_2Br_2$, which is dextrorotatory, non-poisonous, has no bitter taste, and is provisionally called *tribromostrychnine oxide*. The portions soluble in alcohol are combined and purified by precipitating the alcoholic solution with water containing hydrochloric acid; the product is amorphous (it has since been obtained crystalline in very small quantity), optically inactive, non-poisonous, and has a composition approximating to the formula $C_{21}H_{20}O_4N_2Br_2$. The aqueous filtrate, from which the last-mentioned precipitate has been separated, contains a substance which has pronounced basic properties, is levorotatory, and is non-poisonous, but has an intensely bitter taste. C. S.

Alkaloids in the Roots of *Sanguinaria canadensis* TAD. KŹNIEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 235—246).—Sanguinarine, isolated by Dana in 1828 from the roots of *Sanguinaria canadensis*, and proved by Schiel in 1842 to be identical with chelerythrine obtained by Probst from *Chelidonium majus*, has been shown to be a mixture of three alkaloids by Schmidt and his collaborators, who found that the roots of *Sanguinaria* contain five alkaloids, namely, sanguinarine (red salts), chelerythrine (yellow salts), protopine, and β - and γ -homochelidonine (colourless salts). The last two are easily separated from the first three by their solubility in aqueous ammonia, but the separation of sanguinarine, chelerythrine, and protopine presents very great difficulties. The author describes a comparatively simple method which depends on the formation of sparingly soluble salts. The alcoholic extract of the powdered roots is evaporated, and the residue is treated with 5% and with 10% acetic acid. Three-quarters of the mass remains undissolved (*P*), and is worked for sanguinarine as described below. The acetic acid solutions are cooled and treated with 40% sulphuric acid, whereby a crystalline precipitate is formed, which is collected after forty-eight hours and yields pure chelerythrine after further purification. The filtrate is cooled in a freezing mixture, and just basified with ammonia. The resulting precipitate is extracted with hot dilute acetic acid, and the solution is

treated with an excess of 40% sulphuric acid. The yellow, crystalline precipitate obtained yields a further quantity of chelerithrine, whilst the filtrate by treatment with ammonia gives a violet precipitate. This is dissolved in 10% acetic acid, and the solution treated with an excess of sulphuric acid. A third precipitate is thus obtained containing a considerable quantity of chelerithrine and sanguinarine; the precipitate obtained by adding ammonia to the filtrate is dissolved in 10% sulphuric acid, and the solution is treated with more sulphuric acid, whereby a fourth crystalline precipitate containing chelerithrine and sanguinarine is obtained, the filtrate being worked for protopine, which is finally isolated in the form of its hydrochloride.

The residue (*P*) is ground with kieselguhr and heated for three hours with 20% sulphuric acid. The red solution deposits a scarlet precipitate on cooling, from which pure sanguinarine is obtained by further purification. The fact that the residue requires prolonged heating with sulphuric acid for solution is taken as evidence that sanguinarine is present in the roots in the form of a stable compound which yields the alkaloid by hydrolysis.

From his analyses the author concludes that sanguinarine separates from solutions containing alcohol in crystals containing $\text{Et}\cdot\text{OH}$; the m. p. of such crystals is 212° . Sanguinarine forms a *periodide*, $\text{C}_{25}\text{H}_{17}\text{O}_4\text{N}_2\text{HI}$, m. p. 205° , and chelerithrine, a *periodide*, $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}_2\text{HI}$,

m. p. 225° , crystallising in ruby-red needles.

C. S.

Reactions of 2:4:6-Trihydroxypiperidine Trisulphite. JULIUS SCHENKEL (*Ber.*, 1910, 43, 2597—2601).—The additive compound of pyridine and sodium hydrogen sulphite, which is regarded as the trisulphite ester derived from 2:4:6-trihydroxypiperidine (compare Bucherer and Schenkel, *Abstr.*, 1908, i, 452), can be estimated by boiling with alkali hydroxide solution and titrating the ammonia evolved. It also reacts with a solution of *p*-nitrobenzenediazonium chloride in the presence of an excess of sodium hydrogen carbonate, yielding a blood-red solution, which changes to yellow on the addition of a slight excess of acid; in acid solution a voluminous, yellow precipitate is obtained, which decomposes rapidly, yielding a resinous product free from sulphur.

Benzoyl chloride and alkali react with the ester, yielding benzoic anhydride, and a hot solution of the ester rapidly transforms phenylhydrazine into its *N*-sulphonic acid.

When boiled with alkalis, the ester yields ammonia, alkali sulphite, and glutacetaldehyde, the last of which was isolated as its dianilide, $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}$ (compare Zincke, *Abstr.*, 1904, i, 448; Koenig, *ibid.*, i, 817), the hydrochloride of which crystallises in red needles, m. p. $141\text{--}143^\circ$.

When the ester is neutralised with sodium hydroxide solution, and then boiled with phenylhydrazine for three hours, ammonia is evolved, and the sodium salt of 1-anilino-2:4:6-trihydroxypiperidine trisulphite, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_3\text{Na}_3\cdot 2\text{H}_2\text{O}$, is obtained as colourless crystals, which begin to decompose at 180° .

J. J. S.

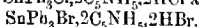
The Action of Sulphites on Pyridine. FRITZ REITZENSTEIN and WILHELM BREUNING (*Ber.*, 1910, 43, 2939—2940. Compare Schenkel, preceding abstract).—A claim for priority. The existence of Zincke's glutacanaldehyde, which Schenkel has isolated in the form of its dianilide, had already been demonstrated by the authors, who obtained from it the ditoluidide (Brouning, *Diss.*, Würzburg, 1909).
R. V. S.

Additive Compounds of Mercury Salts and Aromatic Bases. WILHELM STARONKA (*Bull. Acad. Sci. Cracov.*, 1910, 372—398).—The great solubility of mercury salts in organic bases is due to the formation of additive compounds of the salts and the solvent. The salts of mercury which have been examined are the cyanide, chloride, bromide, and iodide; the bases used are aniline, pyridine, and quinoline. Exactly weighed amounts of a salt and a base are heated in a sealed tube until fusion is complete. The tube is allowed to cool until crystals, generally of an additive compound, separate, and is then carefully re-heated until only a pair of crystals remain; the temperature at which the two crystals persist unchanged for a long time is taken as the temperature of solidification of the mixture under examination. The results are expressed graphically, the molecular concentrations of one constituent being plotted as abscissae, the corresponding temperatures of solidification as ordinates. The curves obtained are of two types, one kind exhibiting a maximum corresponding with the m. p. of the additive compound, and the other kind showing breaks, indicating the transition of one solid phase into another. The compositions of the additive compounds can be determined directly from curves of the first type. In the case of mixtures giving curves of the second type, it is necessary to isolate the solid phase before its composition can be determined by analysis. The isolation is a matter of some difficulty, because the solid phase is only stable within a definite range of temperature; a method is described by which the separation can be effected by the use of a centrifugaliser in an air-bath. Of the bases examined, pyridine shows the greatest tendency to form additive compounds; of the salts, the cyanide. The most frequently occurring types of additive compounds are $\text{HgX}_2 \cdot 2\text{B}$ and $\text{HgX}_2 \cdot \text{B}$, where $\text{B} = 1$ mol. of the base. The following now additive compounds have been obtained: $\text{Hg}(\text{CN})_2 \cdot 6\text{C}_5\text{NH}_5$; $\text{Hg}(\text{CN})_2 \cdot 3\text{C}_5\text{NH}_5$; $2\text{Hg}(\text{CN})_2 \cdot 3\text{C}_5\text{NH}_5$; $\text{Hg}(\text{CN})_2 \cdot \text{C}_5\text{NH}_5$; $\text{HgBr}_2 \cdot \text{C}_5\text{NH}_5$, m. p. 123° ; $3\text{HgBr}_2 \cdot 2\text{C}_5\text{NH}_5$, m. p. 134° ; $\text{HgI}_2 \cdot \text{C}_5\text{NH}_5$, m. p. 90° ; $\text{Hg}(\text{CN})_2 \cdot 3\text{C}_9\text{NH}_7$; $\text{HgBr}_2 \cdot 2\text{C}_9\text{NH}_7$; $\text{HgI}_2 \cdot 2\text{C}_9\text{NH}_7$; $\text{Hg}(\text{CN})_2 \cdot 4\text{PhNH}_2$ (metastable); $\text{HgBr}_2 \cdot \text{PhNH}_2$, m. p. 124° .
C. S.

Theories of the Constitution of Double Salts. PAUL PFEIFFER [with B. FRIEDMANN and H. REKATE] (*Annalen*, 1910, 376, 310—344). The constitution of the double salts formed by metallic halogenides has been explained by various theories, of which the Blomstrand-Remsen and the Werner are the most prominent. According to the former, the constitution is represented by, for example,

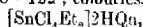
$\text{Cl} \rangle \text{P} \langle \begin{smallmatrix} \text{Cl}:\text{Cl}:\text{Cl} \\ \text{Cl}:\text{Cl}:\text{Cl} \end{smallmatrix}$, the addition occurring by means of tervalent halogen atoms, whilst the constitution is expressed by $[\text{PtCl}_6]\text{K}_2$ by the well-known Werner theory.

The following compounds have been prepared in order to differentiate between these two theories. They are double salts of tin halogenides, all of the type SnA_n , but containing different numbers of halogen atoms, and alkali halogenides or similar compounds. According to the Blomstrand-Remsen theory, the number of molecules of alkali halogenide added is a function of the number of halogen atoms in the tin halogenide; by the Werner theory the number added is independent of the number of halogen atoms in the tin halogenide. The existence of compounds, such as $\text{SnPh}_3\text{Cl}_2 \cdot 2\text{C}_6\text{NH}_5 \cdot 2\text{HCl}$ and



is contrary to the Blomstrand-Remsen theory.

Pyridinium stannichloride, $2\text{Py} \cdot \text{H}_2\text{SnCl}_6$, obtained from pyridine and stannic chloride in concentrated hydrochloric acid, and *quinolinium stannichloride*, $2\text{Qn} \cdot \text{H}_2\text{SnCl}_6$ ($\text{Qn} = \text{C}_9\text{H}_7\text{N}$), m. p. 266° , similarly prepared, form colourless crystals; the *stannibromides*, $2\text{Py} \cdot \text{H}_2\text{SnBr}_6$ and $2\text{Qn} \cdot \text{H}_2\text{SnBr}_6$, m. p. $258-261^\circ$, are yellow. *Pyridinium stannii-iodide*, $2\text{Py} \cdot \text{H}_2\text{SnI}_6$, prepared from pyridine hydriodide and stannic iodide in alcoholic hydrogen iodide, forms dark brown leaflets (compare Rosenheim and Aron, Abstr., 1904, ii, 411. The substance described by these authors as forming bluish-black needles is pyridinium periodide, HPyI_3). *Pyridinium stannimethylpentachloride*, $[\text{SnCl}_5\text{Me}]2\text{HPy}$, and the *quinolinium salt*, $[\text{SnCl}_5\text{Me}]2\text{HQn}$, m. p. 200° (decomp.), obtained from methylstannic acid and pyridine or quinoline in cold concentrated hydrochloric acid, form colourless crystals. *Pyridinium stannimethylpentabromide*, $[\text{SnBr}_5\text{Me}]2\text{HPy}$, m. p. $165-172^\circ$ (decomp.), and the *quinolinium salt*, $[\text{SnBr}_5\text{Me}]2\text{HQn}$, m. p. $80-145^\circ$ (decomp.), obtained from alcoholic tin methyl bromide and pyridine or quinoline in concentrated hydrobromic acid, crystallise in yellow needles. Stannimethylpentaiodides cannot be prepared. *Pyridinium stannidimethyltetraochloride*, $[\text{SnCl}_4\text{Me}_2]2\text{HPy}$, m. p. $143-144^\circ$, and the *quinolinium salt*, $[\text{SnCl}_4\text{Me}_2]2\text{HQn}$, m. p. 167° , obtained from tin dimethyl chloride (m. p. 108° , not 90°) and pyridine or quinoline hydrochloride in methyl-alcoholic hydrogen chloride, form colourless needles. The corresponding *stannidimethyltetrabromide*, $[\text{SnBr}_4\text{Me}_2]2\text{HPy}$, m. p. $108-112^\circ$, and $[\text{SnBr}_4\text{Me}_2]2\text{HQn}$, m. p. 134° , prepared in a similar manner, are colourless, but gradually become yellow by keeping. The following six compounds are also prepared in a similar manner: $[\text{SnCl}_4\text{Et}_2]2\text{HPy}$, m. p. $118-122^\circ$, colourless prisms;



m. p. $134-135^\circ$, stable, colourless needles; $[\text{SnBr}_4\text{Et}_2]2\text{HPy}$, m. p. $90-99^\circ$, colourless needles; $[\text{SnBr}_4\text{Et}_2]2\text{HQn}$, m. p. $120-124^\circ$, colourless needles; $[\text{SnCl}_4\text{Pr}^a]2\text{HPy}$, m. p. 114° , colourless plates; $[\text{SnBr}_4\text{Pr}^a]2\text{HPy}$, m. p. $100-114^\circ$, colourless leaflets. *Pyridinium stannidiphenyltetraochloride*, $[\text{SnCl}_4\text{Ph}_2]2\text{HPy}$, m. p. 186° , obtained from stannic diphenyl oxide and pyridine hydrochloride in saturated methyl- or ethyl-alcoholic hydrogen chloride, and the *quinolinium salt*, $[\text{SnCl}_4\text{Ph}_2]2\text{HQn}$, m. p. $133-140^\circ$, similarly prepared, form colourless

crystals. The corresponding *bromo-compounds*, $[\text{SnBr}_3\text{Ph}_3]_2\text{HPPy}$, m. p. 195° , and $[\text{SnBr}_3\text{Ph}_3]_2\text{HQn}$, m. p. $119-129^\circ$ or $130-131^\circ$ (different samples), are likewise colourless. *Pyridinium stannitriphenyltrichloride*, $[\text{SnClPh}_3]_2\text{HPPy}$, m. p. $169-170^\circ$, obtained from stannic triphenyl chloride (m. p. $112-113^\circ$, not 106°) and pyridine hydrochloride in methyl-alcoholic hydrogen chloride, and *pyridinium stannitriphenyltribromide*, $[\text{SnBr}_3\text{Ph}_3]_2\text{HPPy}$, m. p. $146-153^\circ$ or, after resolidification, 194° , similarly prepared, form colourless crystals, and are the only substances which can be obtained from tin halogenides of the type SnR_3Cl . C. S.

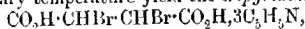
Betaines of Pyridinium-maleic and Pyridiniumacrylic Acids and their Salts. PAUL PREIFFER and A. LANGENBURG [in part with Miss BIRENCKWIG] (*Ber.*, 1910, 43, 2926-2939. Compare O. Lutz, following abstract).—When dibromosuccinic acid is treated with pyridine, a mixture of pyridino salts is obtained, which, on warming, evolves carbon dioxide, and leaves a residue from which two substances can be isolated. Of these, one contains ionic bromine, has acid properties, and is identical with the compound obtained from pyridine and α -bromoacrylic acid. To it is therefore ascribed the structure of α -pyridiniumacrylic acid bromide, $\text{C}_5\text{H}_5\text{N}^+\cdot\text{Br}\cdot\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{H}$. The other substance yields an additive product with hydrogen bromide, which, on heating, loses carbon dioxide and is converted into α -pyridiniumacrylic acid bromide, so that it probably has the structure of a betaine of pyridinium-maleic acid, $\text{C}_5\text{H}_5\text{N}^+\cdot\text{C}(\text{CH}_3)\cdot\text{CH}\cdot\text{CO}_2\text{H}$ or $\text{O}\cdot\text{CO}$

$$\text{C}_5\text{H}_5\text{N}^+ \text{---} \begin{array}{c} \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{O} \cdot \text{CO} \cdot \text{CH} \end{array}$$

, the maleic structure being more probable than

the fumaric, because quinoline and dibromosuccinic acid yield quinoline bromomaleate. The salts described give with alkalis yellow solutions, becoming blood-red (compare the colour reactions of dinitrophenyl pyridinium salts: Zincke, *Abstr.*, 1907, i, 625).

Dibromosuccinic acid and excess of pyridine on standing for two days at the ordinary temperature yield the *tripyrindine* salt,



as a white powder, which when kept over sulphuric acid loses pyridine, forming the *monopyridine* salt, $\text{C}_4\text{H}_4\text{O}_4\text{Br}_2\cdot\text{C}_5\text{H}_5\text{N}$, which after crystallisation forms colourless needles, m. p. about 143° (with evolution of gas).

Pyridine bromomaleate, $\text{C}_4\text{H}_3\text{O}_4\text{Br}\cdot\text{C}_5\text{H}_5\text{N}$ (from bromomaleic acid in ethereal solution), is a white, crystalline precipitate, m. p. $94-100^\circ$. *Pyridine bromofumarate*, $\text{C}_4\text{H}_3\text{O}_4\text{Br}\cdot\text{C}_5\text{H}_5\text{N}$, may be prepared in the same way.

Quinoline bromomaleate, $\text{C}_4\text{H}_3\text{O}_4\text{Br}\cdot\text{C}_9\text{H}_7\text{N}$, is obtained on heating dibromosuccinic acid for some hours with quinoline; it forms colourless needles, m. p. $114-115^\circ$ (with evolution of gas), and yields bromomaleic acid on treatment with ammonia.

The betaine of *pyridinium-maleic acid* is obtained by heating dibromosuccinic acid with pure pyridine for one hour at $60-70^\circ$. The

α-pyridiniumacrylic acid bromide, which is also produced, is removed by the addition of a little water, in which it is very soluble. The betaine becomes brown at 195°. Sodium carbonate dissolves it with evolution of carbon dioxide. When the substance is dissolved in concentrated hydrochloric acid and evaporated on the water-bath, *pyridiniummaleic acid chloride*, $C_5H_5NCl \cdot C(CO_2H) : CH \cdot CO_2H$, is obtained; it crystallises in small white colourless tablets, which decompose at 150° with evolution of gas, having become brown a few degrees previously. The *bromide* may be obtained similarly, or, better, (1) by adding the betaine to concentrated hydrobromic acid until the salt separates out; (2) by evaporating over soda-lime a solution of the betaine in concentrated hydrobromic acid. It forms colourless, prismatic crystals, which decompose at 170°. On heating it to 110°, *α*-pyridiniumacrylic acid bromide is obtained.

α-Pyridiniumacrylic acid bromide is also obtained by warming pyridine with dibromosuccinic acid (*v.s.*), bromomaleic acid, bromofumaric acid, *αβ*-dibromopropionic acid, or *α*-bromoacrylic acid. It forms colourless needles, m. p. 216° (decomp.). With moist silver oxide it gives the betaine in solution. It gives precipitates with potassium dichromate, gold and platinum solutions. *α*-Pyridiniumacrylic acid chloride, $C_5H_5NCl \cdot H_2O$, is prepared from the bromide by the action of moist silver oxide followed by hydrochloric acid; it forms colourless needles, m. p. 195° (decomp.). The *platinichloride*,

$(C_5H_5O_2N)_2PtCl_4 \cdot 4H_2O$, darkens on heating, and decomposes at 196°. The *platinichloride*, $(C_5H_5O_2N)_2PtCl_4 \cdot 4H_2O$, decomposes at 200°. The *picrate*,

$C_5H_5O_2N \cdot O \cdot C_6H_3(NO_2)_3$, has m. p. about 158° (decomp.).

R. V. S.

Characteristic Reaction of Maleic Acid. OSCAR LUTZ (*Ber.*, 1910, 43, 2636—2641).—Anhydropyridiniumsuccinic acid (pyridine-aminosuccinic acid, Abstr., 1901, i, 8) is also formed when *dl*-bromosuccinic acid is treated with pyridine under the conditions described by Dubrenil (Abstr., 1904, i, 189), and is the substance described by Dubreuil as pyridine hydrogen fumarate. The anhydro-compound can also be obtained from maleic acid, for example, (a) when pyridine hydrogen malcato is heated at its melting point (165°) for 15—20 minutes; (b) by keeping an aqueous-alcoholic or methyl alcoholic solution of pyridine and maleic acid at the ordinary temperature for several weeks.

Anhydropyridiniumsuccinic acid, $C_5H_5N \begin{matrix} \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \text{O} \cdot \text{CO} \end{matrix}$ or $C_5H_5N \begin{matrix} \text{O} \cdot \text{CO} \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{matrix}$, has m. p. 192°, and its solubility in water at 18° is 1.65.

This reaction of maleic acid with pyridine is used as an argument in favour of the structural formula $\text{CO}_2\text{H} \cdot \text{CH} \begin{matrix} \text{O} \\ \text{CH}_2 \end{matrix} \text{CO}$, for maleic acid,

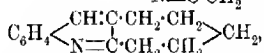
J. J. S.

Conversion of Hydrogenised Carbazoles into Derivatives of 2-Aminodiphenyl. JULIUS VON BRAUN (*Ber.*, 1910, 43, 2879—2888).—In the form of their benzoyl derivatives, the hexahydrocarbazole compounds obtained by the reduction of the corresponding tetrahydrocarbazoles, prepared from cyclohexanones by Fischer's indole synthesis, are readily ruptured by phosphorus pentachloride. Thus hexahydrocarbazole is converted into its benzoyl derivative, b. p. about 270°/10 mm., which yields 20—25% of 2-benzoylamino diphenyl when heated with phosphorus pentachloride, first on the water-bath and finally at 120°. In a similar manner, 1-benzoyl-4-methylhexahydrocarbazole yields 2-benzoylamino-4'-methyldiphenyl, $C_6H_4Me \cdot C_6H_4 \cdot NH \cdot Bz$, m. p. 122°.

CS

Tricyclic Quinolines. WALTHER BORSCHKE [with R. SCHMIDT, H. TIEDTKE, and W. ROTTSIEPER] (*Annalen*, 1910, 377, 70-123).—Quinoline derivatives containing a third ring condensed on the pyridine nucleus in positions 2:3 or 3:4 have been prepared by the three following methods: 1. Condensation of primary arylamines with semicyclic ketones obtained from alicyclic ketones and esters, 2. Condensation of alicyclic ketones containing the grouping $-\text{CO}\cdot\text{CH}_2-$ with *o*-acylanilides. 3. Condensation of isatic acid with alicyclic ketones to acids of the desired bases, and subsequent elimination of carbon dioxide.

The products, for example, $C_6H_4 \begin{matrix} CH:C\cdot CH_2 \\ N=C\cdot CH_3 \end{matrix} > CH_2$ and

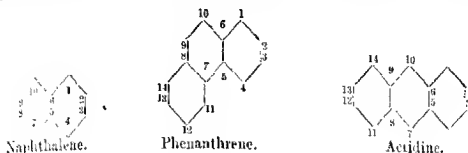


are regarded as 2:3-disubstituted quinolines, and are termed 2:3-trimethylenequinoline and 2:3-pentamethylenequinoline. The corresponding tetramethylene compounds are regarded as derived from tetrahydroacridine.

The general nomenclature of cyclic systems is discussed. The Greek capitals *gamma* Γ , *tau* T , and *pi* Π are suggested for a bridge, an acetylene linking, and a diagonal linking respectively; piene is thus 1-methyl- $\Gamma^{2,4}$ -dimethylmethylenecyclohexene, camphane is 1-methyl- $\Gamma^{1,4}$ -dimethylmethylenecyclohexane, tropan is $\Gamma^{1(4)}$ -methylimino-cycloheptane, thujone is 1-methyl-4-isopropyl- $\Pi^{4(6)}$ -cyclohexan-2-one, and Moyocho and Zienkowski's tricyclene (Abstr., 1905, i, 711) is 1:1-dimethyl- $\Gamma^{2,5}$ -methylenecyclo- $\Pi^{3,7}$ -cycloheptane.

The following considerations are of importance in the numbering of the atoms of ring systems. 1. The system should indicate as far as possible the analogies in the structure of closely related compounds, for example, anthracene, xanthon, and acridine, phenanthrene and phenanthridine, etc. 2. The system should admit a numbering of the analogous reduced cyclic compounds without any alterations in the relative numbering of the substituents. The conditions would be fulfilled by the following system. The cyclic system is so written that as many directly condensed rings as possible lie on a straight line. Each atom of a ring system is numbered, including, for example (unlike the system adopted in Richter's *Lexikon der Kohlenstoff-Verbindungen*), the carbon atoms common to two rings in the naphthalene, anthracene, and similar systems.

The numbering begins at the top of the ring on the extreme right (that is, the atom in the ortho-position to the second ring), and each atom of the first ring is numbered before proceeding to the second ring; for example:



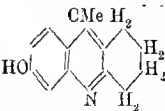
This re-numbering is not followed in the abstract.]

Hydroxymethylenecyclohexanone (Wallach, Abstr., 1904, i, 105) is best prepared by the action of sodium wire on a mixture of *cyclohexanone* and *isoamyl formate*. It has b. p. $87^{\circ}/14$ mm., and tends to resinify when kept. With aniline, it yields *α-ketohexahydrobenzylidene aniline*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}\rangle\text{CH}\cdot\text{CH}\cdot\text{NPh}$, which crystallises from alcohol

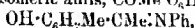
in yellow needles, m. p. 154° . Heating with concentrated sulphuric acid transforms this compound into *α-ketohexahydrobenzylideneaniline-p-sulphonic acid*, $\text{C}_{13}\text{H}_{15}\text{O}_3\text{NS}$, which can also be obtained by condensing hydroxymethylenecyclohexanone with aniline-*p*-sulphonic acid in the presence of *N*-potassium hydroxide. It forms yellow needles, m. p. $261\text{--}263^{\circ}$, yields an *ammonium salt* in the form of yellow plates, and a *potassium salt* in the form of rhombic crystals, m. p. $269\text{--}270^{\circ}$ (decomp.).

α-Ketohexahydrobenzylidene-m-aminophenol, $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$, prepared by condensing the components in glacial acetic acid solution, crystallises in yellow needles, m. p. $172\text{--}173^{\circ}$. Neither of the above condensation products yields a quinoline derivative.

Acetylcyclohexan-2-one, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\text{--CO} \\ \text{CH}_2\text{--CH}_2 \end{smallmatrix}\rangle\text{CHAc}$, prepared by the condensation of *cyclohexanone* and ethyl acetate with sodium, is best isolated as its *copper derivative* in the form of a greenish-grey, crystalline powder, m. p. $160\text{--}161^{\circ}$. The free ketone is a colourless oil with b. p. $97\text{--}98^{\circ}/11$ mm., and can be kept for some time. It condenses with *m*-aminophenol in glacial acetic acid solution, yielding the *m-hydroxyanil*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_9\text{Ac}$, as yellow needles, m. p. $186\text{--}187^{\circ}$, which react with concentrated sulphuric acid at 100° , yielding the quinoline derivative, *5-methyl-8-hydroxy-1:2:3:4-tetrahydroacridine* (*5-methyl-1-hydroxy-2:3-hexamethylenequinoline*: annexed formula). The *sulphate* crystallises from dilute alcohol in yellowish-white needles, m. p. 225° , and the free base crystallises in glistening plates, which darken at 240° , but are not completely molten at 360° ; its solutions have a yellowish-green fluorescence.

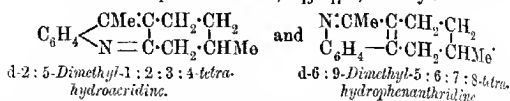


Aniline and *d*-4-acetyl-1-methylcyclohexan-3-one react at 150° , yielding a mixture of isomeric anils, $\text{COMe}\cdot\text{C}_6\text{H}_8\text{Me}\cdot\text{NPh}$ and



or the tautomeric enolic forms. A mixture of the two has b. p.

211°/14 mm., and cannot be separated; the mixture, when heated for three hours with concentrated sulphuric acid on the water-bath, yields a mixture of the two quinoline bases, $C_{15}H_{17}N$, namely:

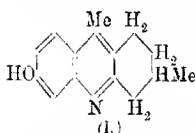


A mixture of the two has b. p. 200°/14 mm., and the separation is based on the fact that the former yields a sparingly soluble hydrochloride and the latter a sparingly soluble dichromate. The acridine base crystallises from light petroleum in colourless needles, m. p. 72–74°, and $[\alpha]_D + 57.07^\circ$. Its solutions in acids have a greenish-yellow fluorescence. The *picrate* forms a yellow, crystalline powder, m. p. 193°; the *methiodide*, $C_{16}H_{20}NI$, crystallises from alcohol in yellow needles, m. p. 232–233°; the *platinichloride*,

$2C_{15}H_{17}N_2H_2PtCl_6$, forms orange-coloured needles, m. p. 213–223°, and the *aurichloride*, $2C_{15}H_{18}NCl_2AuCl_3$, yellow needles, m. p. 166°. The same base can also be prepared by condensing *o*-aminoacetophenone with *d*-3-methylcyclohexanone, and when distilled with zinc dust in an atmosphere of hydrogen yields 2:5-dimethylacridine, $C_{15}H_{15}N$, colourless needles, m. p. 121–122°, the *picrate* of which is sparingly soluble in hot alcohol and has m. p. 225°. A by-product is 2:5-dimethyl-5:10-di-hydroacridine, $C_{15}H_{17}N$, which crystallises from alcohol in colourless plates, m. p. 165–166°.

The dimethyltetrahydrophenanthridene crystallises from light petroleum, has m. p. 78° and $[\alpha]_D + 133.7^\circ$, and its solutions in acids do not fluoresce. The *picrate* has m. p. 208° (decomp.); the *aurichloride*, $C_{15}H_{17}N_2HAuCl_4$, crystallises in yellow needles, m. p.

128°. 9:10-Dimethylphenanthridene, $C_{15}H_{15}N$, is a colourless oil, and yields a *picrate*, m. p. 214°.

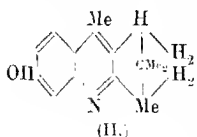


in yellow, crystalline aggregates, m. p. 153–154°, and with sulphuric acid yields 2:5-dimethyl-8-hydroxy-1:2:3:4-tetrahydroacridine

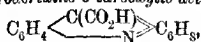
(formula I). This forms greenish-yellow crystals, m. p. 272–273°, and yields a *sulphate* in the form of colourless needles, m. p. 207–208°. When distilled with zinc dust in an atmosphere of hydrogen, the base yields 2:5-dimethylacridine.

d-α-Acetylcamphor-*m*-hydroxyanil, $C_{10}H_{15}Ac \cdot N \cdot C_6H_4 \cdot OH$,

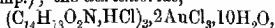
crystallises from alcohol in colourless, flat needles, m. p. 151–152°, and with concentrated sulphuric acid yields the quinoline base, $C_{15}H_{15}ON$ (formula 11). This crystallises in yellow needles, which are unaltered at 360°, and yields a *picrate*.



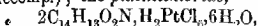
1 : 2 : 3 : 4-Tetrahydroacridine-5-carboxylic acid,



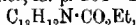
prepared by condensing *cyclohexanone* with *isatin* in the presence of 33% potassium hydroxide and alcohol, crystallises in colourless, glistening plates, m. p. 284—286° (decomp.). The *picrate* forms yellow needles, m. p. 199.5° (decomp.); the *aureichloride*,



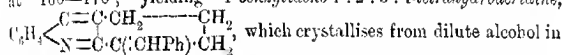
has m. p. 237° (decomp.); the *platinichloride*,



forms glistening, brown crystals, m. p. 222—223°; and the *methyl ester*, $\text{C}_{13}\text{H}_{12}\text{N} \cdot \text{CO}_2\text{Me}$, prepared from the silver salt, has b. p. 200°/24 mm. and m. p. 70°; it yields a *picrate*, m. p. 176—178°, and a *platinichloride*, as red needles, m. p. 204—208°; the *ethyl ester*,



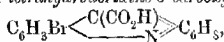
forms broad needles, m. p. 55°, and yields a *picrate*, m. p. 166—167°, a *platinichloride*, $2\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}, \text{H}_2\text{PtCl}_6$, m. p. 193—194°, and an *ethiodide*, $\text{C}_{13}\text{H}_{22}\text{O}_2\text{NI}$, m. p. 168°. 1 : 2 : 3 : 4-Tetrahydroacridine, prepared by heating the carboxylic acid at its m. p., yields a *sulphate*, with m. p. 148°, and a *mercurichloride*, in the form of colourless needles, m. p. 213—214°. The base condenses with benzaldehyde and zinc chloride at 160—170°, yielding 1-benzylidene-1 : 2 : 3 : 4-tetrahydroacridine,



which crystallises from dilute alcohol in glistening plates, m. p. 103—104°. Its *picrate* has m. p. 176—178°. Tetrahydroacridine and phthalic anhydride yield a *phthalone*. When nitrated with 10% nitric acid, the tetrahydro-base yields a mixture of two *nitro-derivatives*, $\text{C}_{13}\text{H}_{12}\text{N} \cdot \text{NO}_2$, namely, dark yellow prisms, melting at 126—130°, and yellow needles, m. p. 138—139°, which have to be separated mechanically. With fuming sulphuric acid at 100°, the base yields *tetrahydroacridine-6-sulphonic acid*, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{NS}$, which crystallises from water in colourless prisms, but at 130—140° the chief product is an isomeric *sulphonic acid*, m. p. 248—250°, together with a small amount of the above sulphonic acid, which is not molten at 300°, and of a *disulphonic acid*.

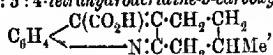
The base reacts with bromine, yielding the *hydrobromide perbromide* $\text{C}_{13}\text{H}_{13}\text{N}, \text{HBr}$, as yellowish-red needles, m. p. 123°.

7-Bromo-1 : 2 : 3 : 4-tetrahydroacridine-5-carboxylic acid,



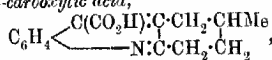
prepared from *cyclohexanone*, 5-bromoisatin, and alkali, crystallises in minute needles, m. p. 274—276°, after drying at 120°. When heated at its m. p., the acid yields 7-bromotetrahydroacridine, $\text{C}_{13}\text{H}_{12}\text{NBr}$, which crystallises from alcohol in flat needles, m. p. 93—94°. The *picrate* crystallises in greenish-yellow plates, m. p. 194—195°, and the *aureichloride* in microscopic needles, m. p. 208°. 7 : 9-Dibromo-1 : 2 : 3 : 4-tetrahydroacridine-5-carboxylic acid, $\text{C}_{14}\text{H}_{11}\text{O}_3\text{NBr}_2$, prepared from 3 : 5-dibromoisatin, crystallises in broad needles, m. p. 242°. 7 : 9-Dibromotetrahydroacridine, $\text{C}_{13}\text{H}_{11}\text{NBr}_2$, crystallises in yellow needles, m. p. 105—107°.

d-2-Methyl-1:2:3:4-tetrahydroacridine-5-carboxylic acid,



obtained from isatin and d-1-methylcyclohexan-3-one, crystallises from glacial acetic acid in yellow needles, m. p. 291—293° (decomp.). d-2-Methyltetrahydroacridine, $\text{C}_{14}\text{H}_{15}\text{N}$, crystallises from light petroleum in colourless, slender plates, m. p. 81—82°, and yields a *picrate*, m. p. 176—177°. The corresponding *dl*-base has m. p. 72—73°, and both the *d*- and the *dl*-base when heated with lead oxide yield 3-methylacridine, the *dichromate* of which forms red needles, m. p. 125—126°.

Isatin and 1-methylcyclohexan-4-one yield 3-methyl-1:2:3:4-tetrahydroacridine-5-carboxylic acid,



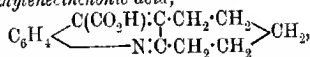
in the form of yellow needles, m. p. 280—281°. 3-Methyltetrahydroacridine, $\text{C}_{14}\text{H}_{15}\text{N}$, crystallises from light petroleum in quadrilateral plates, m. p. 84—85°, and yields a *picrate*, m. p. 194—195°. When heated with lead oxide, the base yields 3-methylacridine (Ullmann, Abstr., 1888, 288).

Pulegone and isatin in the presence of concentrated potassium hydroxide yield α -methyleinchonic acid, together with neutral products, probably owing to the conversion of the pulegone into acetone and 1-methylcyclohexan-3-one.

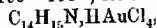
2:3-Trimethylenecinchonic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{CO}_2\text{H})\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{N}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} \text{CH}_3$

obtained from isatin, cyclopentanone, and alkali, crystallises from alcohol or glacial acetic acid in small needles, m. p. 277—278° (decomp.). 2:3-Trimethylenequinoline, $\text{C}_{12}\text{H}_{11}\text{N}$, formed when the acid is heated at its m. p. or by condensing cyclopentanone with *o*-aminobenzaldehyde, crystallises from light petroleum in colourless needles, m. p. 59—60°; the *dichromate* forms sparingly soluble, orange, yellow prisms; the *picrate*, pale yellow needles, m. p. 203—204°; the *aurichloride*, $\text{C}_{12}\text{H}_{11}\text{N}, \text{HAuCl}_4$, needles, m. p. 160—162°; the *platinichloride*, reddish-yellow needles, m. p. 235°; and the *methiodide*, $\text{C}_{12}\text{H}_{11}\text{Nl}$, pale yellow crystals, m. p. 207°.

2:3-Pentamethylenecinchonic acid,



crystallises from glacial acetic acid in glistening needles, m. p. 291—292°, and 2:3-pentamethylenequinoline, $\text{C}_{14}\text{H}_{15}\text{N}$, from light petroleum in colourless needles, m. p. 93·5°; its *hydrochloride* forms broad needles, m. p. 107—108°; its *picrate*, yellow needles, m. p. 197°; its *methiodide* has m. p. 195—196°; its *aurichloride*,



forms yellow needles, m. p. 179°, and its *platinichloride* crystallises with $2\text{H}_2\text{O}$ in orange-red needles, m. p. 214°.

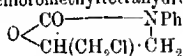
J. J. S.

Oxazole Series. Syntheses of 2-Ketotetrahydro-oxazoles.
TREAT B. JOHNSON and RALPH W. LANGLEY (*Amer. Chem. J.*, 1910, 44, 352—361).—Nemirowsky (Abstr., 1885, 741) has shown that

carbonyl chloride reacts with β -chloroethyl alcohol at 200° to form β -chloroethyl chloroformate. When this ester was treated with aniline, chloroethyl phenylcarbamate, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, was produced, and was converted by alkali hydroxide into 2-keto-3-phenyl-tetrahydro-oxazole, $\text{O} \begin{array}{c} \text{CO}-\text{NPh} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$. Otto (Abstr., 1891, 1373) studied

the action of carbonyl chloride on the dichlorohydrins, and obtained acid chlorides, from which he prepared a series of urethanes. He found that the urethanes from $\alpha\alpha$ -dichlorohydrin yielded ketotetrahydro-oxazoles when they were treated with alkali hydroxide, whilst those from $\alpha\beta$ -dichlorohydrin did not behave in this way. In view of these results, a study has now been made of various halogenalkyl phenylcarbamates and their behaviour towards alkali hydroxide.

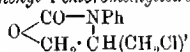
$\beta\beta$ -Dichloroisopropyl phenylcarbamate, $\text{CH}(\text{CH}_2\text{Cl})_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, m. p. 73° , obtained by the action of phenylcarbimide on $\alpha\alpha$ -dichlorohydrin at 100° , crystallises in groups of slender needles, and when heated with potassium hydroxide is converted almost quantitatively into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole,



(Otto, *loc. cit.*).

$\beta\beta'$ -Chlorobromoisopropyl phenylcarbamate, m. p. 73° , obtained by the interaction of phenylcarbimide and $\beta\beta'$ -chlorobromoisopropyl alcohol, crystallises in needles, and is converted by potassium hydroxide into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole.

β -Chloro- γ -bromopropyl phenylcarbamate, m. p. 73° , was prepared from phenylcarbimide and β -chloro- γ -bromopropyl alcohol. γ -Chloro- β -bromopropyl phenylcarbamate, m. p. $75-76^\circ$, is converted by potassium hydroxide into 2-keto-3-phenyl-4-chloromethyltetrahydro-oxazole,



m. p. $73-78^\circ$, which forms groups of needles. A small yield of this oxazole was also obtained by the action of potassium hydroxide on $\beta\beta'$ -dichloropropyl phenylcarbamate. $\beta\beta'$ -Dibromoisopropyl, $\beta\gamma$ -dichloropropyl, and $\beta\gamma$ -dibromopropyl phenylcarbamates have m. p. 73° , $72-73^\circ$, and $77-79^\circ$ respectively. E. C.

Oxazole Series: the Addition of Cyanic Acid to Epichlorohydrin. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1910, 44, 5, 453-466).—Thomsen (Abstr., 1879, i, 217) has described the formation of a ketotetrahydro-oxazole, $\text{C}_4\text{H}_5\text{O}_2\text{NCl}$, from the action of potassium cyanate on epichlorohydrin. The authors have synthesised this substance by the action of strong alkali on $\beta\beta'$ -dichloroisopropyl acetylcarbamate, and thus determined the manner of addition of cyanic acid to epichlorohydrin. It is shown that theoretically three isomeric cyclic compounds might be formed by this addition: 2-keto-5-chloromethyltetrahydro-oxazole, 2-keto-4-chloromethyltetrahydro-oxazole, and γ -chloropropylene imino-carbonate, and that the substance formed must be assigned the structure of the first of these.

$\beta\beta'$ -Dichloroisopropyl acetylcarbamate, $\text{NHAc}\cdot\text{CO}_2\cdot\text{CH}(\text{CH}_2\text{Cl})_2$, crystallises in needles, m. p. 100° .

$\beta\beta'$ -Dichloroisopropyl benzoylcarbamate crystallises in rectangular prisms, m. p. 119° . 2-Keto-3-phenylcarbamyl-5-chloromethyltetrahydro-

oxazole, $\text{CH}_2\text{Cl}\cdot\text{CH}\begin{matrix} \text{O}=\text{C} \\ \text{CH}_2\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh} \end{matrix}$, forms rhombic tablets, m. p. 154 — 155° ; the corresponding 3-benzoylcarbamyl derivative melts at 131 — 132° .

β - γ -Dichloropropyl acetylcarbamate forms prisms, m. p. 64 — 65° .

Allyl acetylcarbamate crystallises in flat prisms, m. p. 64° .

γ -Chloro- β -bromopropyl acetylcarbamate crystallises in prisms, m. p. 60° . γ -Chloro- β -bromopropyl carbamate forms plates, m. p. 93° .

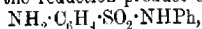
$\beta\beta'$ -Dibromoisopropyl benzoylcarbamate crystallises in plates, m. p. 119° ; the β -chloro- β -bromo-derivative melts at 122° .

β - γ -Dichloropropyl benzoylcarbamate and the corresponding di-bromo-derivative melt at 83° .

γ -Chloro- β -bromopropyl benzoylcarbamate forms tabular crystals, m. p. 113° .

β -Chloro- γ -bromopropyl benzoylcarbamate crystallises in prisms, m. p. 114° . N. C.

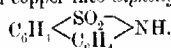
Diphenylene-sultam. FRITZ ULLMANN and CHRISTIAN GROSS (Ber., 1910, 43, 2694—2704).—A sultam could not be obtained from toluene-*p*-sulpho-3-nitro-*p*-toluidide, but one was prepared from *o*-nitro-benzenesulphonanilide, the reduction product of which,



was diazotised, and on the addition of sodium acetate formed

1-phenyl-benzsulphontriazine, $\text{C}_6\text{H}_4\begin{matrix} \text{SO}_2\cdot\text{NPh} \\ \text{N}=\text{N} \end{matrix}$; this was converted

by sodium hydroxide and copper into diphenylene-sultam,



Phenylenenaphthylene-sultam was prepared in a similar manner. Both sultams are colourless, crystalline compounds of strongly acid character. The ring is not opened on heating with hydrochloric acid even under pressure.

Nitro-*p*-toluenesulphonyl-3:5-dinitro-*p*-toluidide, prepared by nitration of *p*-toluenesulphonyl-*p*-toluidide, crystallises in colourless prisms, m. p. 184° . Sulphuric acid converts it into 3:5-dinitro-*p*-toluidine. With methyl sulphate, *p*-toluenesulphonylmethyl-3:5-dinitro-*p*-toluidide is formed in faintly yellow crystals, m. p. 199° .

p-Toluenesulphonyl-3-nitro-*p*-toluidide, produced on nitrating with 18% nitric acid at 60 — 70° , forms yellow prisms, m. p. 101° . It yields 3-nitro-*p*-toluidine when hydrolysed. When reduced with stannous chloride, *p*-toluenesulphonyltolylene-3:4-dianiline is obtained; it crystallises in needles, m. p. 140° ; the hydrochloride forms colourless, silky needles, decomp. 170° . *p*-Toluenesulphonylazirine-toluene forms colourless needles, m. p. 159° . *p*-Toluenesulphonylmethyl-3-nitro-*p*-toluidide has m. p. 124° . *p*-Toluene sulphonylmethyl-3-amino-*p*-toluidide forms colourless, matted needles, m. p. 133° .

Di-p-toluenesulphonyl-3-nitro-p-toluidide forms colourless needles, m. p. 228°; reduction converts it into *di-p-toluenesulphonyl-tolylene diamine*, crystallising in colourless needles, m. p. 192°.

o-Nitrobenzenesulphonanilide has m. p. 115°; *o-aminobenzenesulphonanilide* forms matted needles, m. p. 122°; the *hydrochloride* separates in colourless needles.

Diphenylene-sultam crystallises in well-formed, colourless, lustrous needles, m. p. 196°; it dissolves in ammonia and alkalis with a faint yellow coloration and bluish fluorescence. The mother liquors of the preparation contain *hydroxybenzenesulphonanilide*, colourless needles, m. p. 123°.

1-Phenylbenzsulphontriazine (annexed formula) is amorphous, m. p. 111° (decomp.). The triazine ring is immediately opened by dilute mineral acids, and the clear solutions couple with β -naphthol, forming red azo-dyes.

Diphenylene-N-methylsultam is obtained from *nitrobenzene sulphonmethylanilide*, m. p. 73°, which is reduced by stannous chloride to *aminobenzene-sulphonmethylanilide*, forming colourless crystals, m. p. 63°. The last substance when diazotised, and the diazonium solution evaporated, gives the *sultam* in colourless needles, m. p. 112°.

o-Nitrobenzenesulphonyl- β -naphthalide forms colourless needles, m. p. 158°; on reduction, *o-aminobenzenesulphonyl- β -naphthalide* is formed, crystallising in needles, m. p. 113°.

1- β -Naphthyl-benzsulphontriazine, $C_6H_4 \begin{smallmatrix} N=N \\ \diagup \quad \diagdown \\ SO_2 \cdot N \cdot C_{10}H_7 \end{smallmatrix}$ separates in colourless needles, m. p. 107–108°.

Phenylenenaphthalene-sultam, $C_6H_4 \begin{smallmatrix} SO_2 \\ \diagup \quad \diagdown \\ C_{10}H_6 \end{smallmatrix} NH$, crystallises in colourless needles, m. p. 254°; the solutions fluoresce faintly blue.

E. F. A.

Isomerism of Complex Compounds. I. Asymmetric Complex Compounds of Platinum. IWAN OSTROMISLENSKY and AUGUST BERGMANN (*Ber.*, 1910, 43, 2768–2774; *J. Russ. Phys. Chem. Soc.*, 1910, 42, 611–624).—The object of the authors was

to prepare complex compounds of platinum of the type $\begin{smallmatrix} a \\ b \end{smallmatrix} \begin{smallmatrix} m \\ n \end{smallmatrix} Pt \begin{smallmatrix} m \\ n \end{smallmatrix}$ or

$\left[\begin{smallmatrix} a \\ b \end{smallmatrix} \begin{smallmatrix} m \\ n \end{smallmatrix} Pt \begin{smallmatrix} m \\ n \end{smallmatrix} \right]_{m_2}$ in order to see if optical isomerides are capable of

existence. If this were so it would follow that Werner's explanation of the existence of two isomerides of the formula $Cl_2Pt(NH_3)_2$ is not a correct one. The stable, asymmetric compound, *cis-plato-pyridine-*

amine-chlorosulphite, $\begin{smallmatrix} Cl \\ HO_2S \end{smallmatrix} \begin{smallmatrix} NH_3 \\ \diagup \quad \diagdown \\ Pt \quad \diagdown \quad \diagup \\ NC_5H_5 \end{smallmatrix}$, has been prepared, but

so far no evidence of isomerism has been obtained.

To prepare the above compound, sulphur dioxide is passed into an aqueous suspension of plato-semipyridine-amine-chloride (*Abstr.*, 1886, 857) heated on the water-bath. The amine-chloride dissolves, leaving undissolved a small quantity of a yellow substance (*d*). The filtrate, on concentration, gives clear, colourless, monoclinic crystals

[$\alpha:b:c=0.966:1:0.712$; $\beta=91^{\circ}43'$] of the plato-pyridine-amine-chlorosulphite. With brucine it gives an easily soluble salt or double compound.

The mother liquors from the chlorosulphite sometimes deposit a yellow substance, which is identical with *A*. It is soluble in chloroform, and can thus be separated from the chlorosulphite, which is practically insoluble. It contains the same percentage of platinum and nitrogen as the chlorosulphite, but it is not isomeric or identical with it, as it does not contain sulphur. A formula is not given for it.

Plato-semitylenediamine chloride, $[C_7Pt(NH_2)_2 \cdot C_6H_5 \cdot CH_3]$, was obtained by warming potassium platinumchloride with 1:3:4-tylenediamine. It forms microscopic, yellow needles, with a green tinge, which are insoluble in ordinary solvents. Attempts to prepare an asymmetric complex from it by replacing one of the chlorine atoms by the SO_3H group were not successful. Treatment with sulphites, bisulphites, or sulphur dioxide gave precipitates which were analysed, but to which the authors assign no formula.

Plato-semiisobutylenediamine chloride, as also the asymmetric compound, $\left[\begin{array}{c} H_2C \cdot NH_2 \\ | \\ Me_2C \cdot NH_2 \end{array} \right]_2 Pt(NH_2)_2 \cdot C_6H_5 \cdot CH_3$, are not capable of existence.

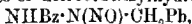
T. S. P.

Nitrosohydrazines, isoAzotates [isoDiazo-compounds], and Azo-compounds of the Aliphatic Series. JOHANNES THIELE (*Annalen*, 1910, 376, 239—268; *Abstr.*, 1908, i, 927).—The main object of the paper is to show that aliphatic *isozotates* (isodiazo-compounds) behave like their aromatic analogues, except, of course, that they do not yield diazonium salts with acids.

The production of *isodiazo*-compounds from a primary hydrazine (or its nitroso-derivative, which has an asymmetric structure), ethyl nitrite, and sodium ethoxide is represented by the scheme: $NHR \cdot NH_2 \rightarrow N(NO)R \cdot NH_2 \rightarrow N_2O + NHR \cdot NO$ (a decomposition resembling that of *sec.-az*-hydrazines by nitrous acid) $\rightarrow RN:N \cdot ONa$. (The formation of Hantzsch and Lehmann's azotates, which are quite different from the *isozotates*, from nitroso-alkylurethanes and very concentrated potassium hydroxide is explained by the intermediate formation of the same primary nitroso-amine, $NHR \cdot NO$. Further research is necessary in order to explain the remarkable difference in the course of the two reactions.)

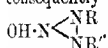
Methylhydrazine sulphate, which is conveniently prepared by heating a benzene solution of benzylideneazine with methyl sulphate for five hours and decomposing the additive product with water, is exactly neutralised by sodium hydroxide, and the solution is treated with three times the calculated amount of 5*N*-nitrite and is made distinctly acid with acetic acid; when the mixture becomes neutral, acetic acid is again added, and so on for about eight hours until the methylhydrazine has been converted into *nitrosomethylhydrazine*, $NO \cdot NMe \cdot NH_2$, m. p. 45° , which is then liberated by sodium carbonate and extracted with ether. Its aqueous solution develops an intense violet coloration with ferric chloride, yields a white precipitate with

mercuric salts, and gives a reddish-brown, crystalline precipitate, and ultimately a reddish-brown coloration, with copper sulphate after the addition of sodium acetate or hydroxide. It reacts with an aqueous suspension of benzaldehyde containing a trace of sulphuric acid to form *nitrosobenzylidenemethylhydrazine*, $\text{CHPh}\cdot\text{N}\cdot\text{NMe}\cdot\text{NO}$, m. p. $77-78^\circ$, with 10% sodium hydroxide and benzoyl chloride to form *benzoylnitrosomethylhydrazine*, $\text{NHBz}\cdot\text{NMe}\cdot\text{NO}$, m. p. $126-127^\circ$ (decomp., rapidly heated), and with $N/2$ -sodium hydroxide and benzenesulphonyl chloride to form *benzenesulphonylnitrosomethylhydrazine*, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{NMe}\cdot\text{NO}$, m. p. 83° ; the last two compounds, like the corresponding derivatives of nitrosobenzylhydrazine,



m. p. $126-127^\circ$, and $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\text{Ph}$, m. p. $115-116^\circ$, do not develop a violet coloration with ferric chloride.

In methylhydrazine the nitrogen atom which is already alkylated is alone attacked by further methylation. Nitrosomethylhydrazine and nitrosobenzylhydrazine, however, readily react with methyl sulphate or benzyl chloride in the presence of aqueous sodium hydroxide, yielding *nitrosohydrazomethane*, $\text{NHMe}\cdot\text{NMe}\cdot\text{NO}$, b. p. $56^\circ/10\text{ mm.}$, *nitroso- α -dibenzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\text{Ph}$, m. p. 69° , *α -nitroso- β -benzyl- α -methylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NMe}\cdot\text{NO}$, m. p. 53° , and *α -nitroso- α -benzyl- β -methylhydrazine*, $\text{NHMe}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\text{Ph}$, m. p. 39° , all of which give intense blue colorations with ferric chloride instead of the violet colorations obtained with monoalkylated nitrosohydrazines. Since the group $\cdot\text{N}\cdot\text{N}\cdot\text{OH}$ cannot be present in these four dialkylated nitrosohydrazines, it follows that this group is also not present in monoalkylated nitrosohydrazines, which therefore cannot have the symmetrical structure $\text{NHR}\cdot\text{NH}\cdot\text{NO}$, in which alone tautomerisation could occur in such a way as to form the group $\cdot\text{N}\cdot\text{N}\cdot\text{OH}$. α -Nitroso- β -benzyl- α -methylhydrazine and α -nitroso- α -benzyl- β -methylhydrazine exhibit very similar properties, but they depress each other's m. p., and the latter is changed into the former by mineral acids; the two substances are not identical, and consequently nitrosodialkylhydrazines cannot have the constitution



Fission into an amine and nitrogen monoxide has been accomplished hitherto only in nitrosohydrazines of the aromatic series. Now it is shown that members of the aliphatic series decompose in a similar manner, by heating nitrosobenzylhydrazine with ethyl oxalate; the resulting amine is isolated partly as *benzylloxamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, m. p. 223° , mainly as *ethyl benzylloxamate*, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, m. p. 48° .

Sodium methylisooxazide, $\text{NMe}\cdot\text{N}\cdot\text{ONa}$, is obtained in slender, white needles by treating methyl-alcoholic nitrosomethylhydrazine with sodium methoxide, ether, and ethyl nitrite; it inflames when heated or when treated with concentrated sulphuric acid, explodes in moist carbon dioxide, yields diazomethane when heated at $130-200^\circ/12\text{ mm.}$, gives in aqueous or alcoholic solution a characteristic reddish-violet coloration with copper acetate, is reduced to methylhydrazine by 8–10% sodium hydroxide and aluminium, and is oxidised to methylnitroamino

by alkaline potassium ferricyanide. The isodiazomethane liberated from the sodium salt changes at once to diazomethane; thus, ordinary acids cause an evolution of nitrogen, benzoic acid produces methyl benzoate, hydrogen cyanide produces methylcarbamylamine, and β -naphthol produces β -naphthyl methyl ether. Sodium benzylisozoxide (*loc. cit.*) is unstable, decomposes in carbon dioxide, yields benzyl alcohol with dilute sulphuric acid, and benzyl β -naphthyl ether with β -naphthol, is reduced to benzylhydrazine by aluminium and 8% sodium hydroxide, and is oxidised by alkaline potassium ferricyanide to benzylnitroamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NO}_2$, m. p. 38—39°, which forms a mercury derivative, $\text{Hg}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$.

s-Dibenzylhydrazine is best prepared by the cathodic reduction of a methyl-alcoholic solution of benzylideneazine containing potassium hydroxide; its dinitroso-derivative has m. p. 44°, and yields *s*-diphenylazomethane when gently warmed in the absence of air. *s*-Benzylmethylhydrazine dihydrochloride, $\text{NHMe}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}\cdot 2\text{HCl}$, m. p. 140° (decomp.), is obtained by boiling either of the nitrosobenzylmethylhydrazines with concentrated hydrochloric acid.

s-Diphenylazomethane (*azotoluene*), $\text{CH}_2\text{Ph}\cdot\text{N}:\text{N}\cdot\text{CH}_2\text{Ph}$, m. p. 31.5°, is obtained by oxidising *s*-dibenzylhydrazine by 3% hydrogen peroxide and 20% ammonium hydroxide; it crystallises in colourless leaflets, and in alcoholic solution is converted into benzylidenebenzylhydrazone by a few drops of hydrochloric acid. In a similar manner, *s*-phenylbenzylhydrazine is oxidised to benzeneazophenylmethane, $\text{NPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$, an orange-coloured oil which readily changes to benzaldehydophenylhydrazone, slowly at the ordinary temperature, rapidly at 200°.

C. S.

Formation of Hydrazones. UGO GRASSI (*Gazzetta*, 1910, 40, ii, 139—153).—The formation of menthonephenylhydrazone from menthone and phenylhydrazine in ethyl-alcoholic solution is complete; it is unimolecular, and the velocity is proportional to the quantity of acid present. In methyl alcohol the velocity is less. The formation of camphorphenylhydrazone could not be followed by the polarimetric method employed for the menthone derivative, but it was found possible to obtain indications that the reaction proceeds three hundred times more slowly than in the case of the latter, when the concentration of acid is the same.

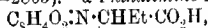
A formula is worked out for the determination of reaction constants based on the measurement of the partition of the phenylhydrazine between two ketones, of which one is optically active. In the case of methyl propyl ketone, methyl isopropyl ketone, and pinacolin, compared in this way with menthone, the following relative reaction constants (K_2/K_1) were found respectively: 5.3, 2.71, 1.29. It follows that the branching of the carbon chain diminishes the readiness of formation of hydrazones.

The author has devised another method founded on the fact that the conductivity of an alcoholic solution of phenylhydrazine and an acid diminishes when phenylhydrazine is withdrawn from the liquid, so that from conductivity measurements it is possible to calculate the quantity of phenylhydrazine remaining in the solution at any time. The solu-

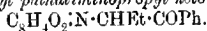
tions employed were 0.022*N* as regards the phenylhydrazine and the ketones, with 0.0065*N*-salicylic acid, and the observed conductivity ranged from 393 (initial) to 43 (final). The following are the reaction constants for the formation of phenylhydrazones of various ketones, the reactions being in all cases complete and unimolecular in the earlier stages: acetone, 0.122; methyl propyl ketone, 0.0228; methyl isopropyl ketone, 0.0114; pinacolin, 0.0043; benzaldehyde, 0.35; salicylaldehyde, 0.416; *m*-hydroxybenzaldehyde, 0.194; *p*-hydroxybenzaldehyde, 0.025; anisaldehyde, 0.061; protocatechualdehyde, 0.019; metocatechualdehyde carbonate, 0.123; piperonaldehyde, 0.048; anillin, 0.060; isovanillin, 0.048. Owing to the rapidity of the reactions, it was necessary to carry out the measurements at 10°. A simple thermostat is described convenient for this purpose, the low temperature being maintained by a supply of ice-water controlled by an electric thermoregulator.

R. V. S.

Derivatives of α -Amino-*n*-butyric Acid. ARNOLD HILDESHEIMER *ibid.*, 1910, 43, 2796—2805).— α -Phthalimino-*n*-butyric acid,

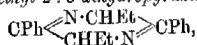


is readily formed when the corresponding ester (Gabriel and Colman, *Abstr.*, 1900, i, 359) is warmed with concentrated sulphuric acid for some three-quarters of an hour, and the mixture poured on to ice. It forms a resinous mass, which can be obtained in a crystalline form only with great difficulty, and then has m. p. 94—95°. The acid reacts with phosphorus pentachloride, yielding the corresponding acid chloride, which condenses with benzene in the presence of aluminium chloride, forming *phenyl phthaliminopropyl ketone*,



The ketone crystallises from light petroleum in colourless, six-sided plates, m. p. 118°, and on hydrolysis with hydrochloric acid yields *phenyl α -aminopropyl ketone hydrochloride*, $\text{NH}_2\cdot\text{CHEt}\cdot\text{COPh}\cdot\text{HCl}$, m. p. 178° after sintering at 170°. The *picrate* has m. p. 174° after sintering at 160°, and the *platinichloride* has m. p. 190—200° (decomp.).

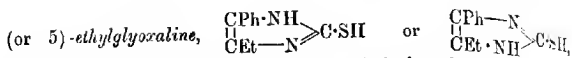
3:6-Diphenyl-2:5-diethyl-2:5-dihydropyrazine,



is formed when an aqueous solution of phenyl aminopropyl ketone hydrochloride is mixed with ammonium hydroxide solution, the flask completely filled with air-free water, corked, and kept overnight. The *hydrochloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{Cl}$, forms a red, crystalline mass, m. p. 167—168° (decomp.).

The base and its hydrochloride are readily oxidised, even on exposure to the air; with dilute nitric acid, oxidation is instantaneous, and the product is Collet's 3:6-diphenyl-2:5-diethylpyrazine. On hydrolysis with hydrochloric acid in an atmosphere of carbon dioxide, the dihydro-base yields mainly phenyl α -aminopropyl ketone, with probably a small amount of the isomeric ketone, $\text{NH}_2\cdot\text{CHPh}\cdot\text{COEt}$ (compare Gabriel, *Abstr.*, 1908, i, 466).

Potassium thiocyanate reacts with an aqueous solution of phenyl aminopropyl ketone hydrochloride, yielding 2-thiol-5(or 4)-phenyl-4



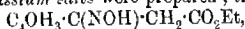
in the form of snow-white needles, m. p. 273° after changing colour at 260° . Nitric acid oxidises the thiol to $\alpha\beta$ -phenylethylthiazole, $\text{C}_{11}\text{H}_{11}\text{N}_2$, m. p. 172° .

α -Phthaliminobutyric acid reacts with red phosphorus and bromine (compare Gabriel, Abstr., 1908, i, 182), yielding $\alpha\beta$ -dibromo- α -phthaliminopropane, $\text{C}_8\text{H}_5\text{O}_2\cdot\text{N}\cdot\text{CHBr}\cdot\text{CHMeBr}$, which crystallises from alcohol in well-developed octahedra, m. p. 147° . When boiled for an hour with water, the bromo-derivative yields phthrlimide, hydrogen bromide (1 mol.), and α -bromopropaldehyde according to the equation: $\text{C}_8\text{H}_5\text{O}_2\cdot\text{N}\cdot\text{CHBr}\cdot\text{CHMe} + \text{H}_2\text{O} = \text{C}_6\text{H}_4\text{O}_2 + \text{HBr} + \text{CHMeBr}\cdot\text{CHO}$. The α -bromopropaldehyde was identified by treatment with sodium acetate and then with phenylhydrazine, when Pinkus' acetolphenylhydrazone (Abstr., 1898, i, 224) was obtained. Hydroxyacetone can be prepared from aminoacetone hydrochloride by the action of nitrous acid, and Nef has shown that it is readily formed from α -hydroxypropaldehyde.

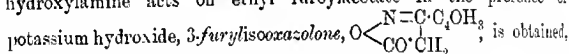
J. J. S.

Furoylacetic Ester and the Furylpyrazolones. III. HENRY A. TORREY and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1910, 44, 5, 391—431. Compare Abstr., 1907, i, 146; 1908, i, 840).—The authors have studied the influence of the furyl group in ethyl furoylacetate and its pyrazolone derivatives, and have synthesised a new analogue of antipyrine containing the furyl group.

An improved method for preparing ethyl furoylacetate is described; the sodium and potassium salts were prepared; the oxime,

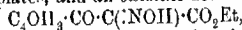


crystallises in long, white, silky needles, m. p. 131 — 132° . When hydroxylamine acts on ethyl furoylacetate in the presence of



crystallising in long, flat needles, m. p. 148 — 149° .

Ethyl furoylacetate forms a semicarbazone, which crystallises in small, flat, rhombic plates, and an oximino-derivative,



m. p. 128 — 129° . By the action of phenylcarbimide, ethyl furoylmalonanilate, $\text{C}_4\text{OH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}$, is produced, crystallising in white needles, m. p. 146 — 150° .

3-Furyl-5-pyrazolone, $\text{C}_4\text{OH}_3\cdot\text{C} \begin{array}{c} \text{N}=\text{NH} \\ \text{CH}_2\cdot\text{CO} \end{array}$, crystallises in small, rectangular plates, m. p. 223° (decomp.); its picrate decomposes at 192° . By the action of acetic anhydride on the pyrazolone, 1-aryl-3-furyl-5-pyrazolone, m. p. 153 — 154° , is obtained; the corresponding 1:2-diacetyl derivative forms long, silky needles, m. p. 103° .

Phenylcarbamylyl furylpyrazolone, $\text{C}_4\text{OH}_3\cdot\text{C} \begin{array}{c} \text{N}=\text{N} \\ \text{CH}_2\cdot\text{CO} \end{array} \text{N}\cdot\text{CO}\cdot\text{NHPh}$, m. p.

192° , is obtained by the action of phenylcarbimide on the pyrazolone,

and 4-benzyliden-3-furyl-5-pyrazolone, $\text{C}(\text{C}_4\text{OH}_3)=\text{N} \begin{array}{c} \text{C}(\text{CHPh})\cdot\text{CO} \end{array} \text{NH}$, by the

action of benzaldehyde. The azo-derivative, 4-benzeneazo-3-furyl-5-pyrazolone, crystallises in red, transparent prisms, m. p. 182—183°.

1-Phenyl-3-furyl-5-pyrazolone hydrochloride, $C_{13}H_{10}O_2N_2 \cdot HCl$, crystallises in small, white needles, m. p. 122—123°. By the action of acetic anhydride on 1-phenyl-3-furyl-5-pyrazolone, 2-acetyl-1-phenyl-3-furyl-

5-isopyrazolone, $C_{14}H_{12}O_2 \cdot C \cdot NAc$, $\begin{matrix} \text{CH}_2 \cdot \text{CO} > \text{NPh} \end{matrix}$, m. p. 69—72°, is obtained in small, flat, slightly yellow prisms. 5-Benzoyloxy-1-phenyl-3-furylpyrazole,

$C_{14}H_{12}O_3 \cdot C \cdot NPh$, $\begin{matrix} \text{CH} \cdot \text{C} > \text{NPh} \\ \text{CH} \cdot \text{C} > \text{OBz} \end{matrix}$, melts at 113—114°, and 4-oximino-1-phenyl-

3-furyl-5-pyrazolone, $C_{14}H_{12}O_3 \cdot C \cdot N$, $\begin{matrix} \text{OH} \cdot \text{N} \cdot \text{C} > \text{CO} \\ \text{CH} \cdot \text{C} > \text{NPh} \end{matrix}$, decomposes at 183—184°.

By the action of benzaldehyde on the pyrazolone, 4-benzylidene-1-phenyl-3-furyl-5-pyrazolone, decomposing at 210—212°, is obtained.

4-Benzeneazo-1-phenyl-3-furyl-5-pyrazolone, $C_{14}H_{12}O_2 \cdot C \cdot N$, $\begin{matrix} \text{N}_2\text{Ph} \cdot \text{CH} > \text{CO} \\ \text{CH}_2 \cdot \text{CO} > \text{NPh} \end{matrix}$, crystallises in long, light red needles, m. p. 165°.

4-β-Naphthaleneazo-1-phenyl-3-furyl-5-pyrazolone crystallises in deep, red needles, m. p. 202—203°. The hydriodide, m. p. 192—193°; the hydrochloride, m. p. 197—198°; the hydrobromide, m. p. 194°, and the picrate, m. p. 157—158°, of 1-phenyl-3-furyl-2-methyl-5-pyrazolone are described. 4-Nitroso-1-phenyl-3-furyl-2-methyl-5-isopyrazolone,

$C_{14}H_{12}O_2 \cdot C \cdot NMe$, $\begin{matrix} \text{NO} \cdot \text{C} > \text{CO} \\ \text{CH}_2 \cdot \text{CO} > \text{NPh} \end{matrix}$, crystallises in green needles, m. p. 185°; its hydrochloride crystallises in bright red needles, decomposing at 189°.

1-p-Bromophenyl-3-furyl-5-pyrazolone, $C_{14}H_{12}O_2 \cdot C \cdot N$, $\begin{matrix} \text{CH}_2 \cdot \text{CO} > \text{N} \cdot C_6H_4Br \end{matrix}$, prepared from p-bromophenyldiazine and ethyl furoylacetate, crystallises in needles, m. p. 160—161°.

3-Furyl-5-pyrazolone 1-benzene-p-sulphonic acid crystallises in small plates, turning brown when kept. 1-m-Nitrophenyl-3-furyl-5-pyrazolone crystallises in yellowish-brown prisms, m. p. 174—175°.

2-Phenyl-3-furyl-4-isopyrazolone, $C_{14}H_{12}O_2 \cdot C \cdot NPh$, $\begin{matrix} \text{CH} \cdot \text{CO} > \text{NH} \end{matrix}$, crystallises in transparent prisms, m. p. 176°.

N. C.

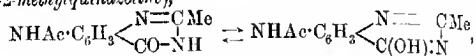
Quinazolines. XXV. Synthesis of 6- and 7-Amino-2-methyl-4-quinazolones from 4- and 5-Acetylaminoacetyl-anthranils. MARSTON T. BOGERT, CARL GUSTAVE ANEND, and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1910, 32, 1297—1312).—4- and 5-Acetylaminoacetyl-anthranils have been prepared by acetylating the corresponding tolylenediamines, oxidising the acetyl derivatives with a neutral solution of potassium permanganate, and treating the resulting diacetylamino benzoic acids with excess of acetic anhydride. The oxidation of 2:5-diacetylamino-toluene proved much more difficult than that of the 2:4 compound, and gave a much smaller yield of the diacetylamino benzoic acid.

When these acetylaminoacetyl-anthranils are condensed with primary

amines, acetylamino-4-quinazolones are produced, and, on eliminating the acetyl group, the 6- or 7-amino-2-methylquinazolones are obtained. Nearly all the quinazolones now described are crystalline solids of high m. p. or b. p.

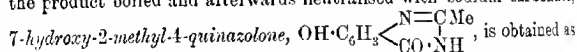
4-Acetylaminoacetylanthranil, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \\ \text{N} \end{smallmatrix} \text{Ac}$, m. p. 220° (corr.), crystallises in colourless needles. 2:5-Diacetylamino-2-oxo-1,4-benzodiazepine-3-carboxylic acid, $\text{C}_6\text{H}_3(\text{NHAc})_2 \cdot \text{CO}_2\text{H}$, m. p. 263° (decomp., corr.), forms minute, colourless crystals. 5-Acetylaminoacetylanthranil, m. p. 253° (corr.), crystallises in needles. The 4- and 5-acetylaminoacetylanthranils absorb moisture, and are re-converted into the corresponding diacetylamino-2-oxo-1,4-benzodiazepine-3-carboxylic acids.

The following quinazolones were prepared from 4-acetylaminoacetylanthranil. 7-Acetylamino-2-methyl-4-quinazolone (4-hydroxy-7-acetylamino-2-methylquinazoline),

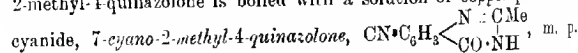


m. p. 344° (corr.), crystallises in slender, silky needles, containing $2\text{H}_2\text{O}$, and when boiled with dilute potassium hydroxide is converted into 7-amino-2-methyl-4-quinazolone (Eger and Kläber, Abstr., 1908, i, 466). The latter compound does not react with phenylhydrazine or ethyl chloroacetate; when boiled with formaldehyde and potassium cyanide, a reaction takes place, but the product does not contain any new substances; its potassium salt, hydrochloride, and platinumchloride are described.

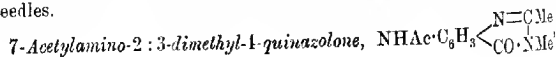
Dinitro-7-acetylamino-2-methyl-4-quinazolone, m. p. 302° (decomp.), forms orange crystals; the nitro-groups probably occupy the 6- and 8-positions. Bromo-7-acetylamino-2-methyl-4-quinazolone, m. p. 292° (corr.), crystallises in minute needles, and, when boiled with 10% potassium hydroxide solution, is converted into bromo-7-amino-2-methyl-4-quinazolone, m. p. 272° — 273° (corr.), which forms light yellow, flaky crystals. 7-Formylamino-2-methyl-4-quinazolone, m. p. 329° — 340° (corr.), forms colourless, feathery crystals, and the corresponding propionyl derivative, m. p. 326° — 327° (corr.), crystallises in long, white, silky needles. When a solution of 7-amino-2-methyl-4-quinazolone in dilute hydrochloric acid is treated with sodium nitrite at 0° and the product boiled and afterwards neutralised with sodium carbonate,



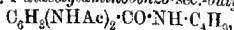
a light brown powder, which darkens at about 345° , but does not melt at this temperature; its acetyl derivative, m. p. 266° (corr.), forms large, pale brown needles. If the diazotisation product of 7-amino-2-methyl-4-quinazolone is boiled with a solution of copper potassium



303° — 304° (corr.), is produced, which crystallises in colourless, feathery needles.

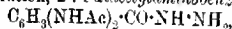


m. p. 281° (corr.), obtained by the action of methylamine on 4-acetylaminoacetylthranil, forms colourless, silky needles. 7-Amino-2:3-dimethyl-4-quinazoline, m. p. 224° (corr.), crystallises in needles or prisms; its *platinichloride* is described. 7-Acetylamino-2-methyl-3-ethyl-4-quinazoline, m. p. 254° (corr.), forms short, colourless needles or lustrous plates. 7-Acetylamino-2-methyl-3-n-propyl-4-quinazoline, m. p. $206-207^{\circ}$ (corr.), crystallises in rosettes of needles. 4-Acetylaminoacetylthranil does not undergo condensation with *sec.*-butylamine, but yields 2:4-diacetylamino-*benzo-sec.-butylamide*,



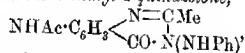
m. p. 235° (corr.), which forms colourless needles. 7-Acetylamino-2-methyl-3-isoamyl-4-quinazoline has m. p. 288° (corr.), and the corresponding 3-phenyl, 3-p-anisyl, 3-p-phenetyl, and 3- α -naphthyl derivatives have m. p. 276° , 273° , 259° , and 256° (corr.) respectively. When 4-acetylaminoacetylthranil is heated with *p*-aminobenzonitrile, a quinazoline is not produced, but a compound, m. p. 258° (corr.), is obtained, containing 12.4% of nitrogen.

When hydrazine hydrate (1 mol.) is boiled with 4-acetylaminoacetylthranil (1 mol.), 3-amino-7-acetylamino-2-methyl-4-quinazoline, m. p. 268° (corr.), is produced, which crystallises with $1\text{H}_2\text{O}$, and fails to give the Bülow condensation (Abstr., 1906, i, 906, 981) with ethyl diacetylsuccinate; the *hydrochloride* has m. p. 312° (decomp.). If 4-acetylaminoacetylthranil is treated in the cold with 50% hydrazine hydrate solution, 2:4-diacetylamino-*benzoylhydrazide*,



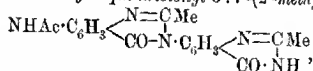
is produced, which crystallises in short, slender needles, and melts at 268° with formation of 7-acetylamino-3-amino-2-methyl-4-quinazoline. 3:7-Diacetylamino-2-methyl-4-quinazoline, m. p. 304° (corr.), forms minute, colourless crystals, and, when boiled with dilute potassium hydroxide, is converted into 3:7-diamino-2-methyl-4-quinazoline, m. p. 238° (corr.), which forms silky needles.

3-Anilino-7-acetylamino-2-methyl-4-quinazoline,



m. p. 214° (corr.), obtained by the action of phenylhydrazine on 4-acetylaminoacetylthranil, forms colourless, feathery needles.

7-Acetylamino-2-methyl-4-quinazolonyl-3:7-(2'-methyl-4'-quinazoline),



n. p. 335° (corr.), obtained by the condensation of 7-amino-2-methyl-4-quinazoline with 4-acetylaminoacetylthranil, crystallises in short, stout, pale yellow needles.

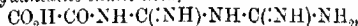
The following quinazolones were prepared from 5-acetylaminoacetylthranil. 6-Acetylamino-2-methyl-4-quinazolone, m. p. 350° (corr.), forms colourless needles or prisms. 6-Amino-2-methyl-4-quinazolone, m. p. $314-315^{\circ}$ (corr.), crystallises in rosettes of needles. 7-Acetylamino-2:3-dimethyl-4-quinazolone, m. p. 278° (corr.), and 7-acetylamino-2-methyl-3-ethyl-4-quinazolone, m. p. 229° (corr.), form colourless, silky needles. The corresponding 3-n-propyl and 3-phenyl

derivatives have m. p. 181° and 255° (corr.) respectively. 3-Amino-6-acetylamino-2-methyl-4-quinazoline, m. p. 262° — 263° (corr.), obtained by heating 5-acetylaminoacetylanthranil with dilute hydrazine hydrate, crystallises in rosettes of colourless, silky needles.

E. G.

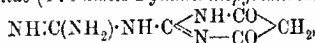
Diguanide and Compounds Derived from It. KAROL RACKMANN (*Annalen*, 1910, 376, 163—183. Compare Bamberger and Dieckmann, *Abstr.*, 1892, 737; Söll and Stutzer, this vol., i, 14).—Diguanide has been prepared by a modification of Herth's method (*Abstr.*, 1881, 896), using soda-water bottles in place of sealed tubes. The sulphate can be obtained from the copper derivative by treatment with 10% sulphuric acid, and the free base from the sulphate by the action of barium hydroxide. Diguanide, $\text{NH}[\text{C}(\text{NH}_2)_2\text{NH}]_2$, crystallises from absolute alcohol in glistening prisms, m. p. 130° , and its aqueous solution decomposes gradually when kept. The carbonate, $\text{C}_2\text{H}_2\text{N}_7\text{H}_2\text{CO}_3$, crystallises in prisms, sparingly soluble in alcohol; the normal hydrochloride, $\text{C}_2\text{H}_2\text{N}_7\text{HCl}$, forms glistening needles, m. p. 235° , and the acid hydrochloride, $\text{C}_2\text{H}_2\text{N}_7\cdot 2\text{HCl}$, large plates, m. p. 248° . The nitrate, $\text{C}_2\text{H}_2\text{N}_7\text{HNO}_3$, crystallises in large, glistening prisms, m. p. 192° ; the acetate, $\text{C}_2\text{H}_2\text{N}_7\text{CH}_3\text{CO}_2\text{H}$, has m. p. 268° , the oxalate, $\text{C}_2\text{H}_2\text{N}_7\text{C}_2\text{O}_4\text{H}_2$, m. p. 210° , and the chloroacetate, m. p. 186° . The cyanoacetate forms soluble, glistening plates, and the succinate, $2\text{C}_2\text{H}_2\text{N}_7\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$, colourless crystals.

Oxalyldiguanide, $\begin{array}{c} \text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH}) \\ \text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH}) \end{array} \rangle \text{NH}$, prepared by the action of ethyl oxalate on diguanide, crystallises from alcohol in large, colourless needles, which decompose above 300° . It does not react with ethyl oxalate or ethyl malonate, but when warmed with dilute hydrochloric acid yields diguanidino-oxalic acid,

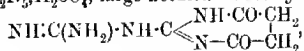


which crystallises in long, thin needles, m. p. 240° . The sodium salt, $\text{C}_4\text{H}_6\text{O}_8\text{N}_5\text{Na}$, forms long needles, and the barium salt, small, sparingly soluble needles.

Malonyldiguanide (4 : 6-diketo-2-guanidinopyrimidine),



prepared by boiling an alcoholic solution of diguanide with ethyl malonate, crystallises in small needles, and has not acidic properties. The hydrochloride, $\text{C}_6\text{H}_6\text{O}_2\text{N}_5\text{HCl}$, forms feathery needles, and the sulphate, $2\text{C}_6\text{H}_6\text{O}_2\text{N}_5\cdot\text{H}_2\text{SO}_4$, large needles. *Succinyldiguanide*,



is only formed in the absence of all traces of water, and has feebly basic properties. The sulphate, $\text{C}_6\text{H}_6\text{O}_2\text{N}_5\cdot\text{H}_2\text{SO}_4$, crystallises in large needles, the hydrochloride, $\text{C}_6\text{H}_6\text{O}_2\text{N}_5\cdot 2\text{HCl}$, in slender needles, and the picrate, $\text{C}_6\text{H}_6\text{O}_2\text{N}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, in brilliant, large needles, m. p. 220° .

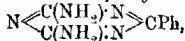
A theoretical yield of ammeline can be obtained by condensing diguanide with an absolute alcoholic solution of ethyl carbonate, and a theoretical yield of thioammeline by condensing diguanide with an alcoholic solution of hydrogen sulphide. The symmetrical constitu-

tional formulae for these two compounds are regarded as established beyond dispute by these syntheses, and also the symmetrical formulae of other cyanuric acid derivatives.

When diguanide is condensed in aqueous solution with carbon disulphide, the product consists of somewhat unstable, reddish-brown crystals, $C_3H_5N_9S_2$.

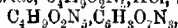
Formylguanamine (1:3-diamino-1:3:5-triazine) (Bamberger and Dieckmann: Abstr., 1892, *loc. cit.*) can be synthesised from diguanide and ethyl formate in absolute alcoholic solution.

Phenylguanamine (3:5-diamino-1-phenyl-1:3:5-triazine),



prepared by the action of benzoyl chloride and alkali on diguanide sulphate, crystallises from water in large prisms, m. p. 222° , and yields a picrate, m. p. 228° .

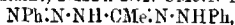
Diguanide reacts with an alcoholic solution of chloroacetic acid, yielding diguanidinouacetic acid, $C_3H_6N_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, in the form of its hydrochloride. The acid crystallises from aqueous alcohol in long needles, and reacts with both acids and alkalis. The sodium salt, $C_3H_5O_2N_3Na$; hydrochloride, $C_3H_5O_2N_3 \cdot \text{HCl}$, and picrate,



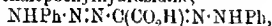
m. p. 202° , are described.

J. J. S

Synthesis of Tetrazoles from Arylazoiimides. OTTO DIMROTH and SIEGFRIED MERZBACHER (*Ber.*, 1910, 43, 2899—2904. Compare Abstr., 1907, i, 659).—Extending to acetaldehydophenylhydrazone and glyoxylic acid phenylhydrazones the reaction with phenylazoiimide previously studied, the authors have been able to isolate *N*-benzeneazacetophenylhydrazidine, $\text{NHPh} \cdot \text{N} \cdot \text{N} \cdot \text{CMe} \cdot \text{N} \cdot \text{NHPh}$ or



and *N*-benzeneazo-oxalophenylhydrazidine,



as intermediate products. The former substance when treated with hydrochloric acid yields benzenediazonium chloride and acetophenylhydrazidine, $\text{CMe}(\text{NH}_2) \cdot \text{N} \cdot \text{NHPh}$. The second product cannot be decomposed in that way, but benzeneazo-5-hydroxy-1-phenyl-1:2:3-triazole (compare Dimroth and Eberhardt, Abstr., 1905, i, 99) is formed when its sodium salt is treated with benzoyl chloride and sodium hydroxide. These hydrazidine derivatives could not be converted into tetrazoles. When, however, tribromophenylazoiimide reacts with the hydrazones mentioned, the intermediate products are labile; they lose tribromoaniline spontaneously, 1-phenyl-4-methyl-1:2:3:5-tetrazole and 1-phenyl-1:2:3:5-tetrazole-4-carboxylic acid being obtained.

N-Benzeneazacetophenylhydrazidine, obtained by heating acetaldehydophenylhydrazone and phenylazoiimide in alcoholic sodium ethoxide solution for forty hours on the water-bath, crystallises in reddish-yellow, rhomboidal tablets, m. p. 101° (with evolution of gas). In contact with dilute hydrochloric acid, it gradually dissolves with evolution of gas, and from the solution acetophenylhydrazidine hydrochloride, $C_8H_{12}N_3Cl \cdot \frac{1}{2}\text{H}_2\text{O}$, can be obtained (compare

Voswinckel, Abstr., 1902, i, 844). It melts at 140° , resolidifies, and melts again (not sharply) at 205° .

The sodium salt of *N*-benzenazo-oxalomonophenylhydrazidine,
 $C_{14}H_{12}O_2N_5Na \cdot 3H_2O$,

is prepared by heating glyoxylic acid phenylhydrazone and phenylazimidide in alcoholic sodium ethoxide solution for fifteen minutes on the water-bath. It is a yellow, crystalline substance, which becomes red in excess of sodium hydroxide in consequence of the formation of a disodium salt. With acids, it yields the free acid as a flocculent precipitant, which soon decomposes with evolution of gas even in the cold.

1-Phenyl-4-methyl-1:2:3:5-tetrazole, $PhN \cdot N \cdot N \cdot CMe \cdot N$, is best freed from the accompanying tribromoaniline by extraction with ether and subsequent distillation in a vacuum, the distillate being collected at $140^{\circ}/15$ mm. It crystallises in long, flat, colourless needles, m. p. 40° , and has an odour of jasmine, although the isomeric 1-phenyl-5-methyl-1:2:3:4-tetrazole (following abstract) has no smell.

R. V. S.

Diazohydrazides. OTTO DIMROTH and GUILLAUME DE MONTMOLIN (*Ber.*, 1910, 43, 2904—2915. Compare preceding abstract).—The diazohydrazides from monoacylhydrazines condense to 1:2:3:4-tetrazoles when treated with alkalis, indicating that they are β -diazohydrazides of the type $NAr \cdot N \cdot NH \cdot NH \cdot CO \cdot R$ (compare Curtius, Abstr., 1893, i, 463). The diazo-derivatives of the diacylhydrazines, also yield tetrazoles with alkalis, an acyl group being eliminated, and in many cases (for example, 5-hydroxy-1-phenyltetrazole) this synthesis offers the best means of preparing tetrazole derivatives. It was not found possible to prepare the bisdiazohydrazides,
 $NAr \cdot N \cdot NAc \cdot NAc \cdot N \cdot NAr$,

from which pentazoles might have been obtained by a method analogous to that described in the preceding abstract. Only monoacyl-diazohydrazides can react with a second molecule of a diazonium salt, and they then undergo a tautomeric rearrangement, such that the reaction product spontaneously decomposes into the diazoamide-compound and the azoimide of the acid group.

Diacylhydrazines do not react with diazonium salts in acid solution. The diazohydrazides are readily obtained as white or yellow, usually flocculent, precipitates, however, when aqueous solutions of the diacylhydrazides are treated with a slight excess of sodium carbonate, and then with the equivalent quantity of the neutralised diazonium chloride solution. The temperature is maintained at -10° , salt being added to prevent freezing. On addition of sodium hydroxide, the precipitate is converted into the tetrazole derivative. 1-Phenyl-1:2:3:4-tetrazole was obtained by the use of diformylhydrazine (the diazohydrazide from which is very unstable), and it has the properties formerly described. 1-*p*-Tolyl-1:2:3:4-tetrazole, $C_6H_5N_4$, forms colourless needles, m. p. 96° . 1-*p*-Nitrophenyltetrazole may be obtained similarly.

1-Phenyl-5-methyl-1:2:3:4-tetrazole, $NPh \cdot N \cdot N \cdot CMe$ (from

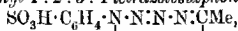
diacetylhydrazine), forms lanceolate crystals, m. p. 97.5° . *p*-Toluenesulphohydrazine, $C_7H_7N_2 \cdot NAc \cdot NHAc$, is more stable than the phenyl derivative. It forms small, pale brown crystals, m. p. 60° (decomp.). 1-*p*-Tolyl-5-methyl-1:2:3:4-tetrazole, $C_8H_{10}N_4$, has m. p. 106° . *p*-Nitrobenzenesulphohydrazine, $C_{10}H_{11}O_3N_5$, forms colourless, lustrous crystals, m. p. 107° (with evolution of gas). It can be preserved unchanged in the dry state for months. 1-*p*-Nitrophenyl-5-methyl-1:2:3:4-tetrazole, $C_8H_7O_2N_5$, crystallises in pale yellow plates, m. p. 129° .

The diazohydrazides from dibenzoylhydrazine are more unstable than those from diacetylhydrazine. It is necessary to dissolve the hydrazine in dilute sodium hydroxide, owing to its slight solubility in water. Benzenesulphobenzoylhydrazine was obtained as a white, unstable precipitate.

5-Hydroxy-1-phenyl-1:2:3:4-tetrazole, obtained from ethyl hydrazinedicarboxylate and benzenediazonium chloride, is identical with the phenylhydroxytetrazole of Freund and Hempel (Abstr., 1895, i, 133).

Tribromobenzenediazonium salts react (but incompletely) with ethyl hydrazinedicarboxylate in weakly acid solution. Ethyl tribromobenzenesulphohydrazinedicarboxylate, $C_6H_2Br_3N_2 \cdot N(CO_2Et) \cdot NH \cdot CO_2Et$, is better obtained in presence of sodium carbonate. It forms small, colourless needles, which explode at $111-115^{\circ}$, according to the rate of heating. The compound can be preserved unchanged. Ethereal hydrogen chloride decomposes it into its components. It was not possible to prepare the corresponding tetrazole.

The monoacylhydrazines react with diazonium salts, not only in alkaline, but also in acid solution. Most of the diazohydrazides are too unstable to be isolated and purified. Benzenesulphohydrazide and *p*-toluenesulphohydrazide are white precipitates, which are rapidly converted into the tetrazoles when treated with sodium hydroxide. *p*-Nitrobenzenesulphohydrazide, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot NHAc$, is soluble in dilute sodium hydroxide with production of an intense, bluish-red coloration, which afterwards disappears, and the tetrazole is formed. With *p*-toluenediazonium chloride in solution containing alkali hydroxide, it yields *p*-nitrobenzenediazoaminotoluene (Bamberger, Abstr., 1895, i, 351), a smell of *p*-tolylazoinide is observed, and azoinide is found in the filtrate. Sulphobenzenesulphohydrazide, $SO_3H \cdot C_6H_4 \cdot N_2 \cdot NH \cdot NHAc$, is obtained by the method described in the form of its sodium salt, which is very stable when dry. Water slowly effects an anomalous decomposition, azoinide and sodium sulphinate being produced. The substance reacts with *p*-toluenediazonium chloride only in the presence of sodium hydroxide, azoinide and sodium *p*-toluenediazoaminobenzenesulphonate being formed. With sodium hydroxide the diazohydrazide yields the sodium salt of 1-phenyl-5-methyl-1:2:3:4-tetrazolesulphonic acid,

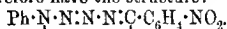


in crystalline form. The silver salt, $C_8H_7O_3N_4SAg$, crystallises in flat, lustrous prisms.

Benzenesulphobenzhydrazide (Curtius, loc. cit.) is converted by sodium

hydroxide into 1:5-diphenyl-1:2:3:4-tetrazole, identical with that of Schröter (Abstr., 1909, i, 617, 773).

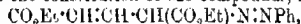
5-Phenyl-1-*p*-nitrophenyl-1:2:3:4-tetrazole, $C_{13}H_9O_2N_5$, is produced in addition to *p*-nitrophenylazoimide and a green sodium salt, *rac*-*p*-nitrobenzeneazohenzhydrazide (von Pechmann, Abstr., 1896, i, 615), is dissolved in sodium hydroxide. It forms yellow prisms, m. p. 149°. The nitrophenylphenyltetrazole, m. p. 177—178°, obtained by Schröter must therefore have the structure:



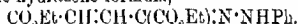
Semicarbazide reacts with benzene and with *p*-toluene-diazonium chlorides in acetic acid solution, yielding crystalline diazohydrazides. The *toluene* derivative is the more stable. It forms colourless laminae, which decompose rapidly even when dry. An ethereal solution, when kept in the cold, deposits carbamazoimide of m. p. 97°, and in the filtrate *p*-toluidine is present. Tolueneazosemicarbazide does not yield the corresponding tetrazole when treated with alkali. The action of a cold alcoholic solution of sodium ethoxide gives rise to sodium azoimide, diazoaminotoluene, *p*-toluidine, and sodium carbonate. Hence it is possible that in this diazohydrazide the azo-group is attached in the α -position.

R. V. S.

Action of Diazo-compounds on Ethyl Glutaconate. FRIEDRICH HENRICH, W. REICHENBURG, G. NACHTIGALL, W. THOMAS, and C. BAUM (Annalen, 1910, 376, 121—151. Compare Abstr., 1899, i, 764; Dimroth and Hartmann, Abstr., 1909, i, 66).—The products obtained by the action of diazonium salts (1 mol.) on ethyl glutaconate are yellow, and have the constitution of azo-compounds, for example,



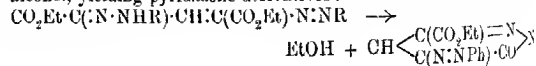
or the tautomeric hydrazone formula,



The fact that they can be boiled with alcohol or even distilled without decomposition and that they do not couple with R-salt indicates that they cannot have the diazo-constitution $>\text{C}(\text{OEt})\cdot\text{O}\cdot\text{N}_2\text{R}$ (compare Dimroth, *loc. cit.*), although it is highly probable that such diazo-compounds are formed as unstable intermediate products in the preparation of the stable azo-compounds.

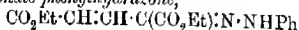
The condensation takes place most readily in an aqueous alcoholic solution of the ester, and in the presence of sodium acetate and aqueous solution of the diazonium salt. The reaction proceeds slowly and is complete in half to one hour.

When an excess of diazonium salt is used, a compound of the type $\text{CO}_2\text{Et}\cdot\text{C}(\text{N}_2\text{Ph})\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NHPh}$ is formed. These compounds are quite different from the formazyl derivatives described previously (Heimich and Thomas, Abstr., 1908, i, 114); they have an intense red colour, and readily lose the elements of ethyl alcohol when heated in alcohol, yielding pyridazone derivatives:

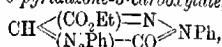


decomposition proceeds at very different rates with the different condensation products, those containing ortho-substituents in the mesene nuclei being most stable. When such substituents are present, the elimination of the alcohol is effected by heating with acetic anhydride, but in the case of the mesitylene derivative, even this reagent is without action. The stability of the compounds depends not merely on the positions of the substituents, but also on their chemical nature, the more electro-positive the ortho-substituent the greater its stabilising effect. The pyridazone derivatives are brown or brownish-yellow solids, the colour being palest when halogen substituents are present in *m*- or *p*-positions; they are stable towards organic acids or aqueous solutions of alkalis, but dissolve in concentrated phosphoric acid, yielding reddish-yellow solutions.

Ethyl glutaconate phenylhydrazone,

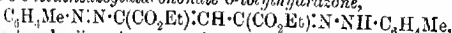


(desmotropic formula), separates from alcohol in long, pale yellow, glistening crystals, *m. p.* 67–68°. *Ethyl 3-benzeneazoglutaconate phenylhydrazone*, $\text{N}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NHPh}$, separates in a boiling mixture of benzene and light petroleum (1:4) in brilliant, glistening, rhombic crystals [*a*:*b*:*c* = 0.4423:1:0.6561], *m. p.* 117° (decomp); it gives Bulow's reaction, and is decomposed to a certain extent when boiled for some time with benzene. *Ethyl 3-benzeneazo-1-phenyl-6-pyridazone-3-carboxylate*,



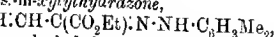
crystallises from alcohol in brownish-yellow needles, *m. p.* 161°.

Ethyl 3-o-toluenazoglutaconate o-tolylhydrazone,



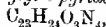
forms dark red, glistening crystals, *m. p.* 131°, after sintering at 130°, the corresponding *ethyl 5-o-toluenazo-1-o-tolyl-6-pyridazone-3-carboxylate*, $\text{C}_{21}\text{H}_{20}\text{O}_5\text{N}_4$, crystallises in dark brown needles, *m. p.* 160°, after sintering at 150°; the isomeric *5-p-toluenazo-1-p-tolyl-6-pyridazone-3-carboxylate* forms pale brown-coloured needles, *m. p.* 157°, and is precipitated readily from *ethyl 3-p-toluenazoglutaconate p-tolylhydrazone*, $\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{H}_3\text{C}$, which resembles the ortho-compound, and has *m. p.* 131°, after sintering at 120°.

*Ethyl 3-benzeneazoglutaconate *as*-m-xyllylhydrazone*,

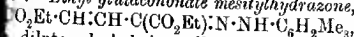


crystallises from dilute alcohol in pale yellow, glistening needles, *m. p.* 107°. *Ethyl m-xyleneazoglutaconate m-xyllylhydrazone*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$, crystallises in glistening prisms, *m. p.* 160–161°.

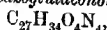
Ethyl 3-mesityleneazoglutaconate 3-carboxylate,



crystallises from alcohol in brilliant, brown prisms, *m. p.* 155° after sintering at 140°. *Ethyl glutaconate mesitylhydrazone*,



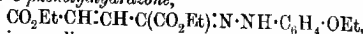
crystallises from dilute alcohol in yellow, glistening crystals, *m. p.* 80°. *Ethyl 3-mesityleneazoglutaconate mesitylhydrazone*,



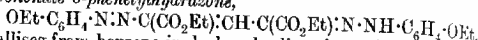
JL. XCV

i.

separates from light petroleum in glistening, red crystals, m. 143—150°, and does not yield a pyridazone derivative. *Ethyl glutacononate o-phenethylhydrazone*,

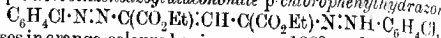


forms glistening, yellow crystals, m. p. 85°, and *ethyl o-phenethylhydrazonate o-phenethylhydrazone*,



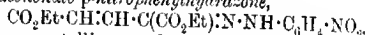
crystallises from benzene in dark red, glistening prisms, m. p. 145°.

Ethyl p-chlorobenzeneazoglutacononate p-chlorophenethylhydrazone,



crystallises in orange-coloured prisms, m. p. 138°, and when heated with alcohol yields *ethyl 5-p-chlorobenzeneazo-1-p-chlorophenyl-6-pyridazone-3-carboxylate*, $\text{C}_{17}\text{H}_{11}\text{O}_4\text{N}_4\text{Cl}_2$, as pale brown needles, m. p. 208—210°, after sintering at 205°. *Ethyl 3-m-bromobenzeneazoglutacononate m-bromophenethylhydrazone*, $\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}_4\text{Br}_2$, also forms orange-coloured crystals, and has m. p. 130°; *ethyl 5-m-bromobenzeneazo-1-m-bromophenyl-6-pyridazone-3-carboxylate*, $\text{C}_{19}\text{H}_{13}\text{O}_4\text{N}_4\text{Br}_2$, forms pale brown microscopic needles, m. p. 149°. The isomeric o-bromo-derivatives of the glutacononate and pyridazone compounds melt respectively at 143—144° and 166—167°, and the p-bromo-derivatives at 146 and 229°.

Ethyl glutacononate p-nitrophenethylhydrazone,



forms a yellow, crystalline powder, m. p. 109°.

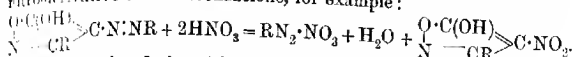
Formyl-α-methylacrylic acid, $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NPh})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, is formed by the action of benzenediazonium chloride (2 mol.) on methylglutaconic acid in dilute acetic acid solution (compare Abstr. 1908, i, 114), and crystallises from alcohol in dark-coloured needles, m. p. 193° (decomp.). It yields a sparingly soluble, reddish-brown, silver salt.

J. J. S.

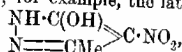
Decomposition of Azopyrazolones by means of Concentrated Nitric Acid. CARL BÜLOW, KARL HAAS, and, in part, with H. SCHMACHTENBERG (*Ber.*, 1910, 43, 2647—2662).—Rothemann's 4-benzeneazo-3-methyl-5-pyrazolone (Abstr., 1895, i, 687) can be prepared by the condensation of hydrazine hydrate with ethyl phenylazoacetate in acetic acid solution. Nitric acid reacts with this pyrazolone, yielding first an additive compound, $\text{C}_{10}\text{H}_{10}\text{ON}_4\cdot\text{HNO}_3$, and finally an orange-yellow nitro-derivative, which has been shown to be 4-p-nitrobenzeneazo-3-methyl-5-pyrazolone, as it can be decomposed from ethyl p-nitrophenylazoacetate and hydrazine hydrate. Further reaction with nitric acid decomposes the nitro-derivative into Betti's 4-nitro-3-methyl-5-pyrazolone (Abstr., 1907, i, 533) and benzenediazonium nitrate. This decomposition proceeds according to the equation: $\text{C}_{10}\text{H}_{10}\text{ON}_4 + 2\text{HNO}_3 = \text{N}_2\text{PhNO}_2 + \text{C}_7\text{H}_5\text{O}_2\text{N}_3$, is used in favour of the azo-structure of the original compound, since Schmidt (Abstr., 1905, i, 951) has shown that true azo-dyes react with concentrated nitric acid, yielding the same compound used in the preparation of the dye, and a nitro-derivative of the compound, which was "coupled" with the diazo-solution.

suggestion that the azo-derivatives of pyrazolone are hydrazones is thus incorrect.

Similarly, the products obtained by the action of diazonium salts on 4-substituted isooxazolones (Claisen and Zedel, Abstr., 1891, 468) are azo-derivatives (*o*-hydroxyazo-compounds), as they are decomposed by nitric acid in acetic acid solution, yielding a diazonium nitrate and a nitro-derivative of the isooxazolone, for example:



Knorr's 4-nitro-1-phenyl-3-methyl-5-pyrazolone (Abstr., 1887, 601) and Betti's 4-nitro-3-methyl-5-pyrazolone are represented by hydroxylic and not ketonic formula; for example, the latter as



since the hydroxylic structure accounts for the pronounced acidic character of these nitro-compounds; for example, their alkali salts are neutral.

The primary product of the condensation of ethyl phenylazoacetate and hydrazine hydrate in cold glacial acetic acid crystallises in glistening, red needles, m. p. 167°; when boiled with alcohol or glacial acetic acid it yields 4-benzeneazo-3-methyl-5-pyrazolone; when boiled with an acetic acid solution of phenylhydrazine it yields 4-benzeneazo-1-phenyl-3-methylpyrazolone, and when heated for a few minutes with an 80% acetic acid solution of benzhydrazide it yields ethyl phenylazoacetate benzoylhydrazone, m. p. 146°. All these reactions indicate that the red compound is to be represented as $\text{N} \cdot \text{H} \cdot \text{CMe} \cdot \text{C}(\text{N}_2\text{Ph}) \cdot \text{CO}_2\text{Et}$.

1-Nitro-5-hydroxy-3-methylpyrazole (4-nitro-3-methyl-5-pyrazolone) crystallises from acetic acid in prisms, m. p. 267° (decomp.), but cannot be acetylated. Its alkali salts are neutral, and hence the hydroxy-compound can be titrated by means of a standard alkali hydroxide solution, using phenolphthalein as indicator. The following salts are described: *potassium*, $\text{C}_4\text{H}_4\text{O}_2\text{N}_3\text{K}$; *ammonium*, yellow needles, decomposing at 248°; *hydrazine*, $\text{C}_4\text{H}_5\text{O}_2\text{N}_3 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, glistening, yellow needles; *barium*, long, golden-yellow, compact prisms; *zinc*, yellow needles; *aluminium*, slender, yellow needles; *silver*, yellow plates, and also *copper*, *lead*, *cobalt*, and *nickel* salts.

4-Benzeneazo-5-hydroxy-3-methylpyrazole reacts with aqueous nitrous acid, yielding 4-benzeneazo-1-nitroso-5-hydroxy-3-methylpyrazole, $\text{NPh} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{C}(\text{OH}) \cdot \text{N} \cdot \text{NO} \\ \text{CMe} = \text{N} \end{array}$, which crystallises in slender

needles, decomposing at 135°. The nitroso-group can be eliminated by warming for a short time with dilute sodium hydroxide solution, with 15% hydrochloric acid, yielding the original hydroxypyrazole. The nitroso-compound is also decomposed when boiled with alcohol, acetic, or glacial acetic acid, and reacts with an excess of nitrous acid, yielding as final product 2:4-dinitrophenol.

When reduced with stannous chloride and hydrochloric acid 4-benzeneazo-5-hydroxy-3-methylpyrazole yields aniline and 4-amino-3-methylpyrazole, but the latter cannot be isolated on

account of the readiness with which it undergoes oxidation into a homologue of rubazonic acid, m. p. 238°.

The same acid is formed, together with a stable product, $C_6H_6O_2N_2$, by the action of oxidising agents on the reduction product of 4-nitro-5-hydroxy-3-methylpyrazole.

4-*m*-Xyleneazo-5-hydroxy-3-methylpyrazole also reacts with nitric acid, yielding 4-nitro-3-methylpyrazolone and *m*-xylenediazonium nitrate.

Nitric acid reacts with ethyl phenylazoacetoacetate, yielding ethyl *p*-nitrophenylazoacetoacetate.

J. J. S.

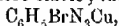
Monosubstituted Triazens and Attempts to Prepare Triazen. OTTO DIMROTH and KARL PFISTER (*Ber.*, 1910, 43, 2757—2767).—By the reduction of phenylazoisimide by stannous chloride in ethereal solution, phenyltriazene is obtained (Dimroth, *Abstr.*, 1907, i, 653). The reaction has been extended to substituted azides, some few of which are more stable than phenyltriazene, but the majority are less stable, decomposing on formation into amine and nitrogen. Benzylazoisimide is much less easily reduced than phenylazoisimide, and the triazen decomposes immediately on formation.

Attempts to reduce azoisimide to triazen by a variety of methods were without success, but it is believed that triazen can exist for a short time in aqueous solution at -10° .

The reductions were carried out at -15° to -18° in dry ether, moisture being carefully excluded; the stannochloride of the triazen crystallises from the mixture, and can be kept without decomposition for some hours in a freezing mixture.

p-Tolylazoisimide is an oil of characteristic anis-like odour, b. p. $80^\circ/10$ mm. *o*-Bromophenylazoisimide is obtained pure on distillation in steam; *o*-bromophenyltriazene is extremely unstable; *m*-bromophenylazoisimide has b. p. $99^\circ/100$ mm.; *m*-bromophenyltriazene is extremely unstable, and explodes on gentle heating.

p-Bromophenyltriazene is more stable; the cuprous compound,



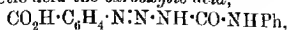
forms yellow crystals, and explodes in the flame. The free triazen separates in long, colourless platelets when freshly prepared, m. p. 36.5° , decomposing into nitrogen and bromoaniline; older samples undergo a change manifested by a visible movement in the crystals, and have m. p. 39° . Solution in ether and precipitation with light petroleum gives the more fusible modification. Generally, *p*-bromophenyltriazene is more stable than phenyltriazene; when brought together with benzaldehyde in ethereal solution at -15° , it decomposes.

2 : 4 : 6-Tribromophenyltriazene could not be obtained from tribromophenylazoisimide.

Similarly, *p*-methoxyphenylazoisimide, which forms crystals, m. p. 36° , does not give a triazen on reduction.

Ethyl *p*-azoisimidebenzoate is volatile in steam, and has b. p. $150^\circ/10$ mm., m. p. 18° . Ethyl *p*-triazenebenzoic acid, $C_6H_4(CO_2Et)_2N_3H$, forms a relatively stable stannochloride. The cuprous salt forms lustrous, golden platelets, decomp. 130° , and can be kept for some months. The free triazen crystallises in lustrous granules or feathery needles, m. p. 68° (decomp.). It combines with phenyl cyanate to an azocarbamide.

$\text{CO}\cdot\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in colourless, lustrous, thin, six-sided plates, m. p. 135° (decomp.). It dissolves in dilute sodium hydroxide with an intense yellow coloration, forming on the addition of acetic acid the *carboxylic acid*,



crystallising in colourless needles, m. p. 172° .

With formaldehyde, the triazen condenses to form a *compound*,



decomp. at 48° to ethyl methylenedi-*p*-aminobenzoate, m. p. 188° .

p-Benzoylphenylazoisimide crystallises in pale yellow, lustrous plates, m. p. 74.5° . The corresponding triazen is relatively stable; it dissolves in ether without the formation of gas, and can be kept in a desiccator for a day.

α - and β -Naphthylazoisimides did not yield triazens on reduction.

E. F. A.

Ionisation, Hydration, and Optical Rotation of White of Egg. WOLFGANG PAULI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 241—243).—The author gives a brief summary of observations which indicate that egg-albumin behaves as a weak amphoteric electrolyte. The properties of acid and alkaline solutions seem to show that the positive and negative albumin ions are combined with a very large number of molecules of water. The hydration which accompanies ionisation gives rise to considerable differences in the optical rotatory power and the viscosity of egg-albumin solutions. The readiness with which albumin ions are formed by different acids is not simply determined by the relative strengths of the acids, although this appears to be the case for the formation of negative ions on addition of different mono-acid bases.

The phenomenon of ionic hydration, which is so strongly developed in the case of albumin, is supposed to be analogous to that of gelatinisation.

II. M. D.

General Protein Chemistry. II. Precipitation of Globulins at the Isoelectric Point. PETER ROSA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1910, 28, 193—199. Compare this vol., i, 646).—It was shown in a previous paper that the sedimentation rate of denatured albumin attains a maximum when the hydrogen ion concentration is that of the isoelectric point, and the same is now shown to be the case for solutions of ordinary (not denatured) serum-globulin, odestin, gliadin, and casein. On this behaviour is based a clear distinction between globulins and albumins; the former are "denaturable" proteins, which, in the ordinary form, precipitate from solution at the isoelectric point, whereas the albumins in the ordinary form are not precipitated by acids, but when denatured also have their sedimentation optimum at the isoelectric point.

The isoelectric constants and relative acidity constants at 18° are as follows: Serum globulin, 0.36×10^{-5} , 2.2×10^3 ; casein from cow's milk, 1.8×10^{-5} , 5.4×10^4 ; gliadin, 6.0×10^{-10} , 6.0×10^5 ; odestin, 1.3×10^{-7} , 2.8, as compared with albumin 0.31×10^{-3} , 1.6×10^3 . Serum-globulin from different animals gave the same values. G. S.

Composition of Nucleic Acid from Yeast. KATHARINA KOWALEVSKY (*Zeitsch. physiol. Chem.*, 1910, 69, 240—264. Compare Levene, Abstr., 1909, i, 54).—Nucleic acid has been prepared from yeast by Altmann's (*Arch. physiol.*, 1899, 526) and by Neumann's method (Abstr., 1899, i, 467; 1900, i, 319), but the product obtained by the latter method is shown to be very impure. The analysis of four specimens prepared according to Altmann gave as a mean $N = 12.52\%$ and $P = 10.02\%$. The low nitrogen value indicates that nitrogenous bases had been removed by acid during the preparation. A specimen prepared on a commercial scale gave $N = 16.16\%$ and $P = 8.65\%$, and this was used for hydrolysis.

When hydrolysed with nitric acid (10 c.c. of nitric acid, D 1.4, + 10 c.c. of water), the products obtained were guanino, 5.16%; adenine, 7.34%; with sulphuric acid (1:2) the products were guanine, adenine, cytosine, and uracil, but no thymine. The uracil is regarded as a secondary product. The nitrogenous portion of the nucleic acid consists of guanine, adenine, and cytosine. The non-nitrogenous portion contains a pento-*c* and not a hexose. The product, C_5H_8O , isolated by Boos (Abstr., 1909, i, 343) in the form of its phenylhydrazone is benzaldehyde, and was present as an impurity in the original phenylbenzylhydrazine used. On the assumption that a molecule of pentose and one of phosphoric acid is present for each molecule of base, the formula $C_{25}H_{42}O_{22}N_{12}P_3$ ($C_5H_5ON_5 + C_5H_5ON_5 + 3C_5H_8O_5 + 3H_3PO_4 = C_{25}H_{42}O_{22}N_{12}P_3 + 6H_2O$) can be deduced. The amounts of bases and pentose actually isolated are less than those required by such a formula, with the exception of guanine. J. J. S.

Guanylic Acid. IVAR BANG (*Zeitsch. physiol. Chem.*, 1910, 69, 167—168).—Polemical. The author defends his formula for guanylic acid, $C_{44}H_{60}O_{34}N_{20}P_3$, against that proposed by Stendel and Brigl, $C_{40}H_{54}O_{30}N_{18}P_3$. W. D. H.

Protamines. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1910, 69, 138—142).—*Crenilabrine* is a new protamine separated from the testes of *Crenilabrus pavo*. It yields arginine nitrogen, 42.3%; lysine nitrogen, 11%, and monoamino-nitrogen, 25.1%. Ammonia, tryptophan, and histidine are absent from its cleavage products. It gives Millon's reaction, so tyrosine is probably present. It is therefore not so simple as salmine.

Malenik has prepared sturine from the Caspian sturgeon; the material appears to have suffered in transport, and Malenik has somewhat modified the author's method; he, moreover, found adenine among the cleavage products, which was not the case with sturine made from German sturgeons. W. D. H.

Lipoids. XIV. Leucopoliin. SIGMUND FRÄNKEL and HERBERT ELIAS (*Biochem. Zeitsch.*, 1910, 28, 320—329).—From the acetone extract of human brain, a new phosphatide named *leucopoliin*, was separated. It is crystalline, and of constant composition, the formula of its cadmium compound being $C_{371}H_{720}O_{74}N_{10}P_2Cl_4Cd$. It is a dec-amino-diphosphatide, or a penta-amino-monophosphatide. It contains no

a ethyl group, and yields no base of the choline group. It contains a carbohydrate acid nucleus. It occurs in about equal quantities in white and grey matter, hence its name.

W. D. H.

Invertase. HANS VON EULER, E. LINDBERG, and K. MELANDER (*Zeitsch. physiol. Chem.*, 1910, 69, 152—166).—A certain quantity of yeast always yields the same amount of invertase whether the dried material is extracted with water, or autolysis is allowed to occur. The preparation of invertase obtained in autolysis contained N 0.36%, C 42.3%, and ash 2.07%. It is the most active preparation so far obtained. If 0.05 gram is dissolved in 5 c.c. of 0.5*N*-sodium dihydrogen phosphate, and 20 c.c. of 20% sucrose solution are added, rotation 0° is reached at room temperature (20°) in fourteen minutes.

W. D. H.

Enzymes of Diastase. L. M. LJALIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 624—633).—The enzymes in various kinds of malt were obtained by precipitation with ammonium sulphate, and the activity of the various preparations in the breaking down of starch was determined as follows: 10 c.c. of a 10% emulsion of starch were placed in a test-tube, the latter immersed in boiling water for half a minute and shaken. After cooling to 20°, a given quantity (0.1, 0.2 . . . c.c.) of the diastase preparation was added, the tube well shaken, and left for half an hour at 20°; 1/2 c.c. of magenta is now added, and the tube inverted. The starch in the tubes in which the magenta is spread evenly through the solution has been completely broken up. The diastase precipitated with ammonium sulphate is always more active than that precipitated with alcohol, and the diastase from air-dried malt, green malt, and the light-coloured malts employed in the manufacture of light beer are the most active, whilst that from dark malt dried at a high temperature is least active.

The fermenting, coagulating, and proteolytic enzymes as well as the oxydases in the diastase obtained from these and other substances are all of the same order of activity according to the source from which they are prepared.

Z. K.

The Deviation of Ferment Action from the Unimolecular Law, with Especial Reference to the Esterases. GEORGE PIERCE (*J. Amer. Chem. Soc.*, 1910, 32, 1517—1532).—The rate of hydrolysis of ethyl butyrate under the influence of lipase has been measured at 37° for different concentrations of the ester and the enzyme. In some experiments the progress of the reaction was found to be in satisfactory agreement with the equation for a unimolecular change, but this is not generally the case, and the actual course in a particular experiment appears to be determined by the relative concentrations of ester and enzyme. Another factor which is of importance is the acid produced by the hydrolysis, for this apparently diminishes the activity of the enzyme.

In solutions which contain the same amount of ester and acid, the time required for the hydrolysis of a given quantity of ethyl butyrate is inversely proportional to the concentration of the enzyme. For

given enzyme and acid concentrations, the time required for the decomposition of the same amount of ester is independent of the ester concentration, provided that this exceeds a certain limiting value. It thus appears that the activity of the enzyme is independent of the ester concentrations where this is varied between considerable limits.

To account for the observations, it is supposed that the enzyme combines with the ester to form an intermediate compound, the amount of which is proportional to the concentrations of the free enzyme and the ester. This compound then undergoes hydrolysis in accordance with the mass action law.

It is shown that the observed facts are consistent with this hypothesis, and that the action is similar to that which probably takes place in the inversion of sucrose under the influence of invertase.

H. M. D.

Benzophosphide. PERCY N. EVANS and JENNIE TILT (*Amer. Chem. J.*, 1910, 44, 361—365).—EVANS and Vanderkleed (*Abstr.*, 1902, i, 273) have described dichloroacetyl phosphide,

$$\text{CHCl}_2\cdot\text{CO}\cdot\text{PH}_2$$

and an account is now given of the preparation and properties of benzoyl phosphide, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{PH}_2$. In view of the analogy of these compounds to the amides, it is suggested that they would preferably be termed "dichloroacetophosphide" and "benzophosphide."

Benzophosphide, prepared by treating benzoyl chloride for six weeks with a current of dry phosphine, generated by the action of phosphorus on alcoholic potassium hydroxide, forms a slightly yellow, or sometimes white, powder. It does not give a definite m. p., but begins to decompose at about 125°. When heated in a current of dry nitrogen, it gradually decomposes above 75° with evolution of phosphine. It is slowly attacked by water or moist air.
 E. G.

Action of Arsenic Acid on Gallic Acid. LEO F. ILJIN (*J. pr. Chem.*, 1910, [ii], 82, 451—462).—Walden, (*Abstr.*, 1899, i, 212) supports Schiff's statement that digallic acid is one of the products of the reaction between gallic and arsenic acids in 95% alcoholic solution. The author has repeated Walden's experiment, but cannot obtain digallic acid, the product free from arsenic being separable by ethyl acetate and petroleum into two fractions, neither of which exhibits the properties of digallic acid; one fraction consists of gallic acid, the other (the smaller) of ethyl gallate.

With regard to the organic arsenic compounds formed in the preceding reaction, the author's results differ from those of Biginelli (*Abstr.*, 1909, i, 801). The arsenical substance obtained by the author in the preceding experiment can be separated, in aqueous ethereal solution, into two fractions by the addition of sodium chloride, one of which does, and the other does not, yield a precipitate with a solution of gelatin. The former is still under investigation; the latter is obtained, after purification, in long needles of the composition $(\text{C}_9\text{H}_9\text{O}_2)_3\text{AsO}$.
 C. S.

General and Physical Chemistry.

Solutions. I. Relations between Density and Refractive Index in Binary Mixtures. F. SCHWERS (*Bull. Soc. chim.*, 1910, [iv], 7, 875-882).—Pulfrich's formula, $(D - D_v)/D = a(N - N_v)/N$, expressing the relationship between change of volume and change in refractive index from the calculated values for any binary mixture of liquids, does not admit of an absolute comparison between the two changes, since in devising the formula Pulfrich introduced the density value in arriving at the refractive index contraction, N_v . The author suggests instead the relation: $C_n = AC_v$, where $C_n = 100(n - n_v)/n$, n being the observed refractive index of the mixture and n_v the calculated value, and $C_v = 100(D - D_v)/D$, D being the observed specific gravity and D_v the calculated value. The value of A has been determined for mixtures of water with alcohol, acids, aldehydes, ketones, glycols, hydroxy-acids, esters, ethers, amines, cyclic compounds, etc., and from the results obtained the following conclusions are drawn. The value of A for a mixture of two given liquids is independent of (1) the concentration of either constituent, (2) the wave-length of the light used, and (3) to a certain extent of the temperature of observation. It is specific for each mixture, and its magnitude is dependent on the molecular volume and structure of each constituent.

These observations lend no support to the "hydrate" theory of solution, since if "hydrates" were formed it is inconceivable that A would be independent of the concentration of each constituent in a given binary mixture.

When a substance undergoes change in volume (by compression, polymerisation, or fusion), the change in refractive index exhibits a relation to the change in volume, which is peculiar to each substance and depends on its constitution.

T. A. H.

Fluorescence and Band Spectra of Oxygen. WALTER STEUBING (*Ann. Physik*, 1910, [iv], 33, 553-584).—It has been found that oxygen exhibits three banded emission spectra, one of which lies in the region extending from the red to the greenish-yellow rays, whilst the others are in the ultra-violet. Detailed observations relating to the three spectra are recorded. The first ultra-violet spectrum, which has usually been attributed to water-vapour by previous observers, is shown to be characteristic of oxygen. The bands of this spectrum, in the neighbourhood of $185\mu\mu$, were repeatedly obtained under conditions which seemed to ensure the absence of water vapour. These conditions were such that the strongest hydrogen lines are not visible, and the author concludes that the first ultra-violet spectrum exhibited by tubes containing oxygen cannot be due to water vapour.

The experimental data are discussed from the point of view of Stark's electron theory.

H. M. D.

Dispersion of Light by Potassium Vapour. P. V. BEVAS (*Proc. Roy. Soc.*, 1910, 84, A, 209—225).—In continuation of previous experiments (compare Abstr., 1909, ii, 783; this vol., ii, 87) on the dispersion produced by potassium vapour, quantitative measurements have now been made for different wave-lengths. The observed deviations extend over the whole of the visible spectrum and for a considerable distance in the ultra-violet. Strong absorption takes place at the lines of the principal series, and anomalous dispersion is found in the neighbourhood of these lines. This phenomenon has been investigated for seven of the pairs forming the principal series lines. As the pairs in this series get closer together with diminishing wave-length, the dispersion effects can only be seen outside the lines forming a pair, and a lack of symmetry in the dispersion curves is found which corresponds with the different intensities of the lines forming the pair. The quantitative data are discussed in reference to Sellmeier's theory.

In regard to the natural periods which correspond with the series lines, it is suggested that these are not due to the atom itself, but to differentiated forms of the atom exhibiting real differences in physical properties.

H. M. D.

Series Spectrum of Mercury. S. R. MILNER (*Phil. Mag.*, 1910, [vi], 20, 636—642).—It has been found that the photographic records of the spectrum of the mercury are in a vacuum show no trace of the continuous back-ground even when the time of exposure is more than fifty times as long as the normal exposure suitable for registration in the case of the mercury are in air. These records show a large number of lines which have not been observed previously.

The wave-lengths of the lines of the principal series down to $m=16$ in Rydberg's formula, and of the diffuse and sharp series down to $m=16$ and $m=14$ respectively, have been measured. The data are utilised to show the accuracy of Rydberg's empirical law, according to which the difference of the frequency of the convergence limit of the principal series and that of the common limit of the sharp and diffuse series is equal to the frequency of the first line of the sharp series.

The agreement is such as to indicate the absolute accuracy of this law.

H. M. D.

Influence of Pressure on the Absorption of Ultra-red Radiation by Gases. EVA VON BAHR (*Ann. Physik*, 1910, [iv], 33, 585—597).—In continuation of previous measurements (Abstr., 1909, ii, 630) of the dependence of the ultra-red absorption on the pressure, experiments have been made with sulphur dioxide, hydrogen chloride, nitrogen peroxide, ozone, benzene, and methyl alcohol. As in the case of the gases examined previously, the absorption of the first four substances increases as the total pressure on the gas is raised, and tends towards a constant maximum value. For benzene and methyl alcohol, on the other hand, the absorption is independent of the pressure between 5 and 760 mm. The collected data indicate that, in general, the pressure at which maximum absorption is reached diminishes as the size of the molecules of the gas increases.

Experiments with nitrous oxide show that a change of pressure, not only influences the quantity of the absorbed radiation, but also brings about a change in the character of the absorbed rays. This variation in the nature of the absorbed radiation is inconsiderable, except at lower pressures.

H. M. D.

A New Radiant Emission from the Spark. ROBERT W. WOOD (*Phil. Mag.*, 1910, [vi], 20, 707—712).—When a condenser spark passes between aluminium electrodes screened by a metal strip, although nothing is visible to the eye, a photograph, taken with a quartz lens shows that the air round the spark is glowing with ultraviolet light for a very short distance. This was shown not to be due to fluorescence of the air caused by the absorption of Schumann waves, or to scattering of the light of the spark by air or dust. The light given out by the emission is embraced between the wave-lengths of 300 to 310, and its spectrum consists of two broad bands, one very strong, the other weaker, identical with the "water bands" of the oxyhydrogen flame. In addition are three lines at 3576, 3537, and 3569, identical with those attributed by Eder and Valenta to nitrogen in the spectrogram of the spark between wet carbon poles. No difference was observed whether the spark took place in dry or moist air, but in oxygen there was practically no emission, whilst in nitrogen it was much brighter and extended a greater distance. No substance has been found transparent to the emission itself. A jet of oxygen killed the emission, but in a jet of nitrogen the emission shot out much further and was of greater intensity. The emission appears to be shot out with very high velocity, for it is not affected by air currents. The new emission appears of great importance in connexion with the origin of the so-called "water-bands," and it is possible it may be identical with the "Entladungsstrahlen."

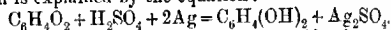
F. S.

Rotatory Power of Tartaric and Malic Acids in Presence of Ammonium Molybdate and Sodium Phosphate. G. MADERNA (*Atti R. Acad. Lincei*, 1910, [v], 19, ii, 130—138).—Seeking an explanation of the phenomena observed in connexion with the precipitation of ammonium phosphomolybdate in the presence of organic acids (this vol., ii, 804), the author has repeated and extended the work of Gernez (*Abstr.*, 1889, 859, 1147), more especially in order to obtain indications as to whether the phosphate radicle enters into the organic complex. He confirms the results of Gernez as regards the rotatory power of tartaric acid in the presence of ammonium molybdate. Rise of temperature affects the rotatory power differently at different concentrations. The concentrations at which a decrease is observed are those at which a precipitation of phosphomolybdate can be effected. Sodium phosphate does not affect the rotatory power of tartaric acid to any marked extent, its influence being in fact no greater than that of sodium or ammonium chlorides. The action of sodium phosphate and ammonium molybdate together is similar to that of the latter substance alone, so that it is probable that the complex substances in solution involve only the acid and the molybdate. The results obtained with malic acid were similar. The author finds reason to doubt the state-

ments of previous workers as to the composition of the complex compounds present in these solutions.

R. V. S.

Action of Quinones and their Sulphonic Derivatives on Photographic Images from Silver Salts. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE and ALPHONSE SEYEWETZ (*Compt. rend.*, 1910, 151, 616—618).—*p*-Benzoquinone and its sulphonic derivative act as "reducing" agents in acid solution towards the negative photographic image. A solution containing 2% of *p*-benzoquinone and 0.5% of sulphuric acid is recommended for use in photography. This bleaches the opaque portions of the image more rapidly than the half tones. The reaction is explained by the equation:



In the presence of an alkali chloride or bromide, however, *p*-benzoquinone produces strong intensification. The effect is less marked in the case of the sulphonic derivative. The solution recommended contains 0.5% of *p*-benzoquinone and 2.5% of potassium bromide. The reaction is represented as: $2\text{C}_6\text{H}_4\text{O}_2 + 2\text{KBr} + 2\text{Ag} + \text{H}_2\text{O} = \text{C}_6\text{H}_4(\text{OK})_2 + \text{C}_6\text{H}_4(\text{OH})_2 + \text{Ag}_2\text{OBr}_2$.

W. O. W.

Temperature-coefficient of the Bleaching of Colouring Matters in the Visible Spectrum. B. SCHWEZOFF (*Zeitsch. Photochem.*, 1910, 9, 65—70).—The influence of temperature on the rate of bleaching of cyanine, pinachrom, pinaverdol, and pinacyanol when exposed to light of known wave-length has been investigated. For a rise of 10° the increase in the rate of bleaching was found to vary from 1.036 to 1.084. These temperature-coefficients are the smallest which have yet been observed in connexion with photochemical changes.

H. M. D.

Acceleration of the Bleaching of Colouring Matters by Aromatic Compounds. GOTTFRIED KÜMMEL (*Zeitsch. Photochem.*, 1910, 9, 54—60).—The increased sensitiveness of colouring matters towards light in presence of certain aromatic compounds has been measured by means of Vogel's actinometer, using specially prepared chromate paper as a comparison standard. Observations were made on cyanine, methylene-blue, and erythrosin, the substances added being anethole, eugenol, *isoeugenol*, safrole, *isosafole*, propenylphenol, and vinylanisole. To obtain comparable results, these were added in such quantity that the molar concentration of the sensitiser in the exposed collodion or gelatin film was in all cases twenty-five times as large as that of the colouring matter. From the tabulated results it is found that safrole and *isosafole* lower the light sensitiveness of all three colouring matters. The other five substances accelerate in general the rate of bleaching, and the sensitising influence of the members of the group increases as the molecular weight decreases.

Experiments are described in support of the view that the bleaching is due to an oxidation process, and that the active substances accelerate the bleaching by acting as oxygen carriers.

H. M. D.

The Probability Variations in the Distribution of α -Particles. ERNEST RUTHERFORD and HANS GEIGER [with a note by H. BATEMAN] (*Phil. Mag.*, 1910, [vi], 20, 698—707).—The object of the experiments was to see whether the rate of emission of α -particles was governed by the laws of probability, or whether the expulsion of one α -particle might not precipitate the disintegration of a neighbouring atom. The scintillations from the α -particles of a polonium source were observed by eye, and recorded on a chronograph tape by closing an electric circuit by hand at the instant of each scintillation. Two thousand scintillations a day were counted for five days, and the chronograph records examined. The differences between the number of scintillations observed, in successive one-eighth, one-quarter, and one minute intervals respectively, and the true average number (total number divided by total number of intervals) were compared with the expression deduced by Bateman from the theory of probability. If x be the true average number of particles observed in any interval, the probability that n α -particles are observed in the same interval is $\frac{x^n}{n!} e^{-x}$. The agreement between theory and experiment was found to be practically perfect, especially for the one-eighth minute intervals, and there is no evidence of greater variations than would be expected from a random distribution. F. S.

Rate of Emission of α -Particles from Uranium and its Products. J. N. BROWN (*Proc. Roy. Soc.*, 1910, A, 84, 151—154).—The number of α -particles emitted from pitchblende films of known weight per unit area has been determined by the scintillations produced in zinc sulphide. For thin enough films the number was proportional to the thickness, so that the total number emitted per gram per second could be calculated. The percentage of uranium in the pitchblende was determined. Per gram of uranium in the pitchblende the number emitted per second was 7.36×10^4 , in fair agreement with the number, 9.25×10^4 , calculated from Rutherford's value for radium. F. S.

The Number of α -Particles Emitted by Uranium and Thorium and by Uranium Minerals. HANS GEIGER and ERNEST RUTHERFORD (*Phil. Mag.*, 1910, [vi], 20, 691—698).—The number of α -particles emitted per second from one gram of uranium, calculated from the number emitted by radium and the ratio between uranium and radium in minerals, is 11,600, if each uranium atom emits one α -particle. On Boltwood's view (*Abstr.*, 1908, ii, 454) that two α -particles per atom are emitted by uranium, and one from each of the subsequent α -ray products, the calculated number of α -particles emitted per second from an old mineral containing 1 gram of uranium is 96,700. The number has been experimentally determined by counting the scintillations produced on a zinc sulphide screen from very thin films of material. The scintillations from uranium are much fainter and more difficult to count than from the uranium minerals and from thorium. Films of pure uranoso-uranic oxide, selected Joachimsthal uraninite, and thorium oxide, five weeks old, from thorite, prepared by Boltwood, were employed. The number of α -particles per second per

gram of uranium or thorium were for these three preparations 23,700, 96,000, and 27,000 respectively. These represent the mean values, corrected for defects of the screen, escape of emanation from the uraninite, and decay of radio-thorium in the thorium oxide. These experiments confirm the view that uranium alone gives two α -particles, all its products giving only one per atom disintegrating. The agreement between the calculated and experimental numbers is closer than could be expected. It was observed that the scintillations from ionium were as bright as, if not brighter than, those from uranium, showing that the range of the α -particle from the latter is not greater than that of ionium (2.8 cm. of air), which is the lowest hitherto measured. A preliminary measurement of the range of the uranium α -particle gave 2.7 cm.

F. S.

The Scattering of Homogeneous β -Rays and the Number of Electrons in an Atom. J. ARNOLD CROWTHER (*Proc. Roy. Soc.*, 1910, A, 84, 226—247).—The fact that β -rays are scattered in a thickness of material far too small to effect the velocity of the rays renders experiments on scattering more simple theoretically than those on absorption. The results are interpreted of the theory of J. J. Thomson (*Camb. Phil. Soc. Proc.*, 1910, 15, v), which is borne out in all points. Homogeneous β rays from a radium source, produced in the manner previously described (compare this vol., ii, 672), are scattered by screens of various materials and thickness, and, by means of stops of various sizes, the scattered rays are confined to a known angle, and pass into an ionisation chamber so shaped that the paths of all rays through it are similar. The following results deduced from the theory were experimentally established: (1) for rays of given velocity and cone of given angle the intensity of the radiation, I , varies with the thickness, t , of material traversed according to the formula: $I/I_0 = 1 - e^{-kt}$, where k is a constant; (2) $\phi/\sqrt{t_m} = \text{constant}$, where t_m is the thickness necessary to cut down to one-half the radiation through a stop of angle ϕ ; (3) $mv^2/\sqrt{t_m} = \text{constant}$, where mv^2 , twice the kinetic energy of the rays, is obtained from the magnetic deflexion. In addition, the results lend themselves to a calculation of the number of electrons in an atom, which is found to be three times the atomic weight for all atoms examined on the assumption that the positive electricity within the atom is not in an electronic condition, but uniformly distributed. An important experiment showed that homogeneous β -rays, when passed through only 0.001 cm. of platinum, are completely scattered, and are then absorbed by aluminium exponentially, whereas the absorption in aluminium alone is quite different, the curve having two inflexions in opposite directions, making the middle part nearly linear, as Wilson found. The view is taken that completely scattered homogeneous β -radiation is exponentially absorbed.

F. S.

Influence of the Temperature on the Change of Radioactive Substances. II. HEINRICH W. SCHMIDT and PAUL CERMAK (*Physikal. Zeitsch.*, 1910, 11, 793—800. Compare Abstr., 1909, ii, 9).—The changes in β -rays from a quartz tube containing radium during

and after heating in a platinum-foil furnace at 1200° to 1300° have been exhaustively examined, and, amid much irregular variation, certain generalities have transpired. The γ -rays throughout in all the experiments show absolutely no definite change in intensity, while the β -rays, on heating the tube, suddenly increase to a maximum, remain constant during the heating (usually one-half to one hour), then, on cooling, very rapidly and steadily decrease to the value before heating, then increase in three hours to the value during heating, and finally, after many days, return to the value before heating. These results are attributed to (1) the gasification of the products radium-*A*, *B*, and *C* by the heating, whereby the absorption of β -rays, which takes place in the radium itself when these products are formed within it, no longer occurs; (2) the sudden adsorption into the mass of the radium again of these products on cooling; (3) the formation in three hours of a new set of products on the walls of the tube and not within the radium, due to the complete expulsion of emanation from the radium during heating; (4) the decay of this emanation with the four-day half-period, and the re-growth of fresh emanation and products within the radium as initially. All the quartz tubes after repeated heatings became porous, and allowed emanation to escape, but some tubes lasted far better than others. The β -rays of uranium-*X* were also examined similarly to those of radium, but apart from initial changes, due to the heat altering the distribution of the substance, no definite changes occurred. The conclusion is arrived at that none of the experiments prove any direct influence of temperature on the rate of transformation of a radioactive substance.

F. S.

The Consequences of the Corpuscular Hypothesis of the γ - and *X*-Rays, and the Range of β -Rays. WILLIAM H. BRAGG (*Phil. Mag.*, 1910, [vi], 20, 385—417).—The paper reviews exhaustively the present state of knowledge of the ionisation, penetration, reflexion, scattering, transformation, etc., of cathode-, *X*-, α -, β -, and γ -rays from the point of view of the "corpuscular" or "entity" hypothesis, which recognises that each type of radiation consists of individual entities, to be followed, each by itself, from its origin through all its changes of direction and sometimes changes of form (conversion of cathode- into *X*-rays, of γ - into β -rays) until its gradually diminishing energy becomes too small to be detected. A method is described of determining the average range of β -rays in various substances, defined as the average weight of substance crossed by the β -ray, when its zig-zag path is straightened out, before it disappears. It is deduced theoretically that the relative ionisations inside similar vessels of different materials, thick enough in the walls to prevent β -rays penetrating them, exposed to a constant stream of γ -rays, gives the relative average ranges of the β -rays in the metals. Results so obtained by H. I. Porter show the greatest range in lead and the least in card. The greater apparent absorption in lead than in other substances is due to the more zig-zag character of the path of the β -ray in lead, the total length of path (in weight units) being actually the greatest in lead. The view is strongly upheld that γ - and *X*-rays do not ionise gases directly at all, but only through first being transformed into

β - or cathode-radiation. The chief evidence against the corpuscular theory is from the work of Barkla on polarisation of X -rays, which, however, is considered a much more simple phenomenon than the polarisation of light, and one not necessarily calling for a wave-motion explanation. The attempt is made to explain the homogeneous secondary X -radiation of Barkla by a double transformation, first of primary X -rays into cathode-rays, and, secondly, the reconversion of the latter into "secondary" X -rays, the existence of a critical speed being assumed, which it is necessary for a cathode-ray falling on an atom to possess in order to produce an X -ray.

F. S.

Typical Cases of Ionisation by X -Rays. CHARLES G. BARKLA (*Phil. Mag.*, 1910, [vi], 20, 370—379).—The relative ionisations in air, carbon dioxide, and ethyl bromide produced by the homogeneous secondary X -rays from twelve elements with atomic weights lying between iron and antimony have been studied. The iron radiation was seventy times more easily absorbed than that from antimony, and throughout the whole range of penetrating power the ionisation in carbon dioxide was proportional to that in air, being about $1\frac{1}{2}$ times greater.

Similar results hold for other gases less dense than carbon dioxide. For ethyl bromide and air the proportionality held for radiations not more penetrating than the bromine radiation. For more penetrating secondary X -rays the relative ionisation of ethyl bromide rises suddenly to over three times its previous value, and then more slowly with increasing penetrating power to between five and six times. These results are similar to those previously found for the absorption of the radiations. Similar variations occur in the ionisations in vapours of methyl iodide, stannous chloride, and selenium chloride at the particular penetrating power characteristic of iodine, tin, and selenium, while carbon, hydrogen, and chlorine give no characteristic secondary X -radiation. No anomalous cases of X -ray ionisation have been observed. The penetrating power of the characteristic secondary X -radiation emitted by the constituent elements of the gas determine the way in which the ionisation depends on the penetrating power of the ionising radiation.

F. S.

The Accumulation of Helium in Geological Time. IV. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, A, 84, 194—196. Compare this vol. ii, 175).—Several examples of Archean rocks show a higher ratio of helium to radioactive matter than thorianite. The minimum age indicated by the helium ratio for sphenes from Archean rocks is about 700 million years. A sphen from the recent volcanic rocks of the Zaacher Sea showed a helium ratio at least two thousand times less. An explanation for the anomalous case of beryl which contains helium out of all proportion to its radioactive content, due to Boltwood, is that in the crystallisation of the beryl one of the longer-lived products of disintegration, as radium, ionium, etc., has separated also, of which after a few thousands of years nothing would be recognisable but the helium to which it had given rise.

F. S.

The Absorption of Radium Emanation by Coconut Charcoal. JOHN SATTERLEY (*Phil. Mag.*, 1910, [vi], 20, 778—788).—The first point tested was whether the same fraction of radium emanation, whatever the amount may be, is absorbed by charcoal when the experimental conditions are the same. For solutions of strengths 3×10^{-9} and 6×10^{-9} gram of radium, but not for stronger solutions, proportionality between the emanation retained and the amount of radium present held good, justifying the method previously employed (*Abstr.*, 1908, ii, 918). With a steady source of emanation the fraction absorbed decreases with the length of the experiment, as though the charcoal became saturated. The humidity of the air stream made no difference. A constant air stream was sent through two charcoal tubes in series. The ratio of the amount of emanation absorbed in the second to that in the first rose with the time of experiment. With tubes 8 sq. cm. in cross section containing 30 cm. length of coarsely powdered coconut charcoal, and an air stream 0.5 litre per minute continued twenty-one hours, 62 per cent. of the total emanation is absorbed. For air streams 0.11, 0.25, and 0.80 litre per minute, the fractions absorbed were respectively 0.86, 0.73, and 0.23. F. S.

The Relation between Uranium and Radium. V. FREDERICK SODDY (*Phil. Mag.*, 1910, [vi], 20, 340—342).—The rate of growth of radium in the three uranium solutions, which previously had proceeded according to the square of the time (compare this vol., ii, 10), has since not been maintained, and it has been found that the constant of the electroscope employed has changed, the instrument now being about 10% more sensitive than at first. Previous estimates of the period of the parent of radium (ionium) are therefore in error, the data still only affording the means of calculating the minimum period of the long-lived intermediate substance, assuming there is but one, and not as proving the production of radium from the uranium. The minimum period from present results is 35,000 years, and the true period may be much greater. A method of obtaining an upper limit for the period from a study of the intensely active ionium preparations separated from thirty tons of pitchblende by the Austrian Government is given. F. S.

The Rays and Products of Uranium-X. II. FREDERICK SODDY (*Phil. Mag.*, 1910, [vi], 20, 342—345).—The preparations of uranium-X previously described (this vol., ii, 10) have now been under observation for periods of a year to eighteen months, and in none has there been any increase of the initial α -radiation present, which is ascribed to an impurity present from the start in the uranium. This is in agreement with the revised estimate for the minimum period of ionium (compare preceding abstract), for if this is greater than 35,000 years the detection of the ionium produced from the uranium-X by means of its α -rays would not be possible with the arrangements employed. The proportion of β -rays in the radiation of uranium possessing an apparent value for H_p above 8640 is given as $1/750$ th. Tests to see whether actinium is produced from the uranium-X pre-

parations have so far given negative results. Actinium is present in all the preparations, but it is ascribed to initial impurities in the uranium.

F. S.

The Ratio between Uranium and Radium in Minerals
 FREDERICK SONNY and RUTH PIRRET (*Phil. Mag.*, 1910, [vi], 20, 345—349).—Determinations are given of the ratio of radium to uranium in autunite and thorianite (compare Mlle. Gleditsch, *Abstr.*, 1909, ii, 714). The ratio for thorianite was found to be only 3% higher than for Joachimsthal pitchblende, while for autunite (of Portuguese origin) it was very low, being only 44.5% of that of pitchblende. The natural explanation is that autunite is of such recent formation that the uranium-radium series is not yet in equilibrium. The specific α -activities of the oxides of uranium separated from autunite, pitchblende, and thorianite were practically the same, which excludes the possible explanation that the variations in the uranium-radium ratio are due to two successive slow α -changes in uranium itself.

F. S.

Selective Photo-electric Effect of Potassium Mercury Alloys.
 ROBERT POHL and P. FRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1910, 12, 697—710. Compare this vol., ii, 379—472).—The photo-electric sensitiveness of potassium amalgams of varying composition has been investigated. Amalgams containing 2.5 to 17.3 atoms % of potassium do not exhibit the selective effect at $\lambda = 436 \mu\mu$ which is characteristic of potassium. This selective action is, indeed, no longer found in the case of either liquid or solid alloys containing as little as 21 atoms % of mercury.

For alloys containing from 17 to 70 atoms % of potassium a selective effect has been found in the neighbourhood of $\lambda = 386 \mu\mu$, and for alloys which contain from 5 to 10 atoms % of potassium it is probable that there is a further characteristic photo-electric effect at about $\lambda = 313 \mu\mu$. The selective effect at $\lambda = 386 \mu\mu$ is supposed to be due, at any rate in the case of the solid alloy, to the compound K₂Hg.

H. M. D.

The Ionisation Produced by the Splashing of Mercury.
 J. J. LONSDALE (*Phil. Mag.*, 1910, [vi], 20, 464—474).—The ions produced by splashing have been usually examined for volatile liquids, and have been found to move with very small velocity. Hence mercury was tried to see if this was due to condensation of vapour on the ions. The results were found to be independent of electrification of the mercury and of its purity, but depended on the nature of the splash-plate. With iron the positive ions were in great excess. Cleaning the plate did not much affect the positive ionisation, but reduced the negative. Platinum gave smaller positive and negligible negative, mercury negligible positive but larger negative, ionisation. The minimum mobility of the ions with iron splash-plate was 0.013 (cm. per volt-cm.) for the positive and 0.004 for the negative. But in the former case the saturation curve showed a second maximum, due either to ions of

smaller mobility or to neutral doublets broken up by the action of the field. The latter explanation was favoured by further experiments, negative ions in some cases being initially absent, but produced in the gas by the application of a field. The negative ions appear to arise altogether from the breaking up of the doublets. By varying the height of fall of the mercury, it was found that no slow positive ions and no negative (therefore no doublets) are produced when the height is below 21.5 cm. The saturation curves, when heated aluminium phosphate or lime was used as the source of the ionisation, showed similar peculiarities for the positive ions. F. S.

Specific Change of the Ions Emitted by Hot Substances. II.

OWEN W. RICHARDSON and E. R. HULBERT (*Phil. Mag.*, 1910, [vi], 20, 545-559. Compare *Abstr.*, 1908, ii, 1009).—The ratio of the charge to the mass for the positive ions emitted by heated metals has been determined for platinum, palladium, gold, silver, copper, nickel, iron, osmium, tantalum, tungsten, brass, "nichrome," and steel. From this the mass of the ion in terms of the hydrogen atom as unity is deduced, on the assumption that unit charge is carried. A correction reducing the values to 0.62 of the experimental is made, because the value for the negative ion from platinum found by the same apparatus and method was wrong to this extent. The general result is to show that the mass of the positive ion from all substances is of the same order, the mean value being 23.3. Some of the substances proved difficult on account of irregularities in the ionisation, and because the initial value was different from the values after some heating. The suggestion is made that the positive ionisation is due to sodium as a common impurity in all the metals. F. S.

Positive Electrification due to Heating Aluminium Phosphate. A. E. GARRETT (*Phil. Mag.*, 1910, [iv], 20, 573-591).—When aluminium phosphate is heated at about 1200°, large numbers of positive ions are emitted, and this phenomenon has been investigated by measuring the conductivity imparted to the surrounding gaseous atmosphere. The emission effect decays with time, and the activity of the substance at any moment can be represented by an expression of the form: $A(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + B(1 - e^{-\lambda_3 t})$. During the first portion of the period of decay, the nature of the surrounding gas and the traces of water present in the active substance have a marked influence on the form of the decay curve. This is no longer evident when the steady state has been reached.

For a given temperature, the current due to the positive ions has a maximum value for a particular pressure; this pressure diminishes as the temperature is raised. At constant pressure the relationship between the current and the absolute temperature can be expressed satisfactorily by means of Richardson's formula.

Measurements of the value of e/m show that the smallest positive ions, which are emitted at the lowest pressures, are comparable in size with the hydrogen atom. In consequence of the high velocity of the ions at low pressure, even in the absence of an external field, a tube

containing strongly heated aluminium phosphate can be used as a rectifier for alternating currents.

Observations are also recorded which seem to show that neutral doublets as well as ions are emitted by the heated substance.

H. M. D.

The Electrical Conductivity of Liquid Alloys. KARL BORNEMANN and PAUL MÜLLER (*Metallurgie*, 1910, 7, 396-402).—Very few data exist as to the electrical conductivity of liquid alloys. The experiments described have been made in glass or quartz tubes, heated in an oil-bath or an electric furnace, according to the temperature required. Iron, platinum, or carbon electrodes are used, auxiliary electrodes being introduced in quartz tubes at different points for the measurement of the fall of potential.

The liquid alloys of sodium and potassium give a conductivity-concentration curve which exactly resembles that typical of a continuous series of solid solutions, such as gold and silver. The conductivity of each liquid metal is lowered by the addition of the other, and the curve has a well-marked minimum. There is no indication of the compound Na_3K , the existence of which is shown on the freezing-point curve as a change of direction, and it therefore appears that this compound is much dissociated in the molten alloys.

On the other hand, liquid alloys of lead and tin exhibit a conductivity which varies with the concentration in an almost perfectly linear manner. The curves of temperature-coefficients of the conductivity follow a similar course to the conductivity curves.

Sodium amalgams exhibit a depression of conductivity at both ends of the series, rising to an intermediate maximum at a point corresponding with the compound NaHg_2 , which probably exists in the liquid in a largely undissociated condition, as evidenced by the very high freezing point of the compound in comparison with those of its components. A similar, but less marked, maximum is caused in the amalgams of potassium by the compound KHg_2 . A new criterion for the existence of compounds in solution is thus obtained.

Observations on dilute amalgams show that the conductivity of mercury is lowered by the addition of either of the alkali metals, but the older observations, that the conductivity is raised by the addition of other metals, are confirmed. The abnormally low temperature-coefficient of mercury (0.001) was attributed by Liebenow to the presence in the liquid of two or more different kinds of molecules, giving it the properties of an alloy. In accordance with this view, the addition of the alkali metals, which form compounds with mercury, and thus increase the number of complex molecules, lowers its conductivity, whilst the indifferent metals, which dissolve in the monatomic form, raise it. It is shown that lead, which has an even lower temperature-coefficient than mercury, has its conductivity raised by the addition of metals which do not combine with it, such as zinc, cadmium, antimony, and bismuth, although the conductivity of bismuth is less than that of lead. Potassium and sodium have a normal temperature-coefficient (0.004), and their conductivity is

lowered by the addition of other metals, whether they form stable compounds or not.

Heterogeneous mixtures of liquid metals, such as lead and zinc, have a conductivity strictly proportional to the concentration, whether the liquids are emulsified or in distinct layers. The temperature at which the separation of a homogeneous liquid alloy into two layers takes place may be determined more accurately by the conductivity than by the thermal method, being indicated by an abrupt change of direction in the conductivity-temperature curve. C. H. D.

The Electrical Conductivity and Hardness of Alloys of Silver and Copper. NIKOLAI S. KURNAKOFF, NIKOLAI A. PUSMIN, and N. SENKOWSKY (*Zeitsch. anorg. Chem.*, 1910, 68, 123-140; *J. Russ. Phys. Chem. Soc.*, 1910, 42, 733-751).—The electrical conductivity and hardness of the alloys of silver and copper have been re-determined with special precautions. The conductivity falls from that of pure copper until 4 atomic % Ag is reached, after which it remains nearly constant until 91 atomic % Ag is reached, and then rises rapidly to that of pure silver. The curve for hard drawn wires closely resembles that for the annealed metals, but the conductivity is throughout lower. The curves representing the temperature-coefficient of the conductivity have exactly the same form.

The determinations of hardness are best made by means of Drinell's ball test on specimens annealed at 650-700°. The curve obtained is the converse of the conductivity curve, and indicates the same limits of concentration of the solid solutions, namely, 0-4 and 91-100 atomic % Ag. The alloys thus represent the simplest type of a series composed of two solid solutions separated by a gap. C. H. D.

Conduction of Electricity Through Solid Silver Chloride. II. MAX LE BLANC and FRITZ KERSCHBAUM (*Zeitsch. Elektrochem.*, 1910, 16, 680-681).—The conductivity of solid silver chloride produced by prolonged treatment with continuous current (this vol., ii, 382) is shown to be due to excessively thin threads of metallic silver. T. E.

Potential of Iron Calculated from Equilibrium Measurements. ARTHUR B. LAMB (*J. Amer. Chem. Soc.*, 1910, 32, 1214-1220).—Richards and Behr (*Abstr.*, 1907, ii, 222) have found that the true potential of iron is 0.18 volt for the porous form, and 0.15 volt for the massive form, the calomel electrode being taken as -0.56 volt, whilst other authors have obtained values about 0.1 volt lower.

A calculation from existing data has now been made, which shows that the potential of iron against a molecular normal solution of ferrous ions is 0.192 volt, the calomel electrode being taken as -0.564 volt. E. G.

Evolution of Gas and Capacity of the Lead Accumulator. FRANZ STREITZ (*Zeitsch. Elektrochem.*, 1910, 16, 747-754).—The quantities of oxygen and hydrogen evolved during the charge of a

small accumulator are compared with those given off from platinum electrodes through which the same current passes. The differences give the capacities of the plates, and these are compared with the capacity of the accumulator when discharged. About 94% of the charge is obtained from the lead plate and about 87% from the lead peroxide plate. It is also shown that the fully charged plates continue to absorb a little hydrogen or oxygen if the charging current is continued. In the case of the lead plate, this is due to occlusion of hydrogen; in that of the lead peroxide plate, it is due to slow oxidation of the lead framework supporting the peroxide.

T. E.

Chemical Action of the Silent Electrical Discharge. A. MOSER and N. ISGARISCHEFF (*Zeitsch. Elektrochem.*, 1910, 16, 613—629).—Various gases are submitted to the action of the silent discharge in ordinary ozone-tubes. The current and the voltage are measured, and also the temperature and pressure of the gas in the tube.

When pure carbon dioxide or a mixture of carbon monoxide and oxygen (2 vols.:1 vol.) is used, an equilibrium is attained which depends on the voltage used, the temperature, and the distance apart of the electrodes. Only traces of ozone are formed, and the same equilibrium is attained in presence of chlorine, but much more slowly. If excess of carbon monoxide or oxygen is used, either the brown solid formed from carbon monoxide alone or ozone is produced. With about 6000 volts at 20° and the electrodes 1.7 mm. apart, about 14% of the carbon dioxide is dissociated when equilibrium is attained. This increases with increased voltage, and diminishes at higher temperatures and with increased distance apart of the electrodes. The quantity dissociated is from thirty to one hundred times more than would be calculated from Faraday's law, but the free energy of the carbon monoxide and oxygen produced is only from 1.2 to 6.3% of the electrical energy expended in producing the decomposition.

The decomposition of hydrogen chloride is very small (about 1% with 14,000 volts).

Sulphur dioxide and oxygen combine quantitatively to form the trioxide. The yield of sulphur trioxide per kilowatt hour varies from 3.5 to 14.3 grams.

A mixture of hydrogen chloride and oxygen is converted largely (95%) into chlorine and water, 10 to 13 grams of chlorine per kilowatt hour being formed.

T. E.

The Oxygen Electrode. Electromotive Behaviour of the Oxides of Platinum. G. GRUBE (*Zeitsch. Elektrochem.*, 1910, 16, 621—632).—The measurements of the potentials of platinum oxide electrodes made by Lorenz (*Abstr.*, 1909, ii, 463, 640, 857) may be too low, owing to the lack of conductivity of the oxides and to the fact that in one set of measurements the electrodes were yielding a small current. The author has made measurements on electrodes containing several grams of the oxide mixed with graphite and compressed in a perforated platinum foil case. The results, referred to the hydrogen electrode for 2*N*-sulphuric acid at 18°, are: PtO₂.4H₂O, 1.06 volts; PtO₂.2H₂O, 1.04 volts; PtO₂, about 1.5 volts; PtO,

indefinite, about 0.9 volt. An electrode containing the trioxide evolves oxygen continuously, and its potential falls slowly. An electrode of the dioxide when polarised anodically behaves in the same way as one made of the trioxide. A monoxide electrode when anodically polarised possesses, at first, a higher potential than the dioxide, which falls off steadily.

The potential of a platinised platinum electrode after anodic polarisation was followed for two hundred and sixty-two days. It fell quite steadily from 1.5 volts to 1.05, at which point it remained for eight days, then falling to 1.02 volts, where it remained without further change.

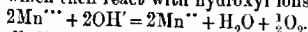
It appears, therefore, that potentials from 1.5 volts downwards are due to solid solutions of PtO_3 in PtO_2 , or of PtO_2 in PtO .

Since platinum electrodes can be polarised up to potentials of 2 volts, it appears probable that an unknown tetroxide of platinum may exist.

T. E.

Anodic Behaviour of Molybdenum, Manganese, Chromium, and Tantalum. HANS KUESSNER (*Zeitsch. Elektrochem.*, 1910, 16, 751-772).—A molybdenum anode dissolves quantitatively, with the valency 6, in *N*-potassium hydroxide. The metal used contained a little iron and traces of carbon and oxide, but two different pieces of it behaved differently. One of them became passive when the current density exceeded about 0.05 ampere per sq. cm., whereas the other showed no signs of passivity with very much larger current densities.

With a manganese anode in neutral solutions (of potassium chloride or sulphate), the metal dissolves, and both hydrogen and oxygen are evolved, the whole of the metal finally present in the solution being bivalent. Manganese itself dissolves with evolution of hydrogen, but the rate is too slow to account for the quantities of hydrogen observed; it is, therefore, thought probable that univalent manganese ions are formed which react with the hydrogen ions in the solution thus: $2\text{Mn}^+ + 2\text{H}^+ = 2\text{Mn}^{++} + \text{H}_2$. From 8-10% of the manganese dissolves in this way. The oxygen is evolved when the potential of the manganese anode is more than 0.3 volt more negative than the normal hydrogen electrode, whilst hydroxyl ions could only be discharged directly if it were 1.62 volts more positive; the oxygen is, therefore, a secondary product. The potential measurements show further that the dissolution of manganese accompanied by evolution of oxygen at the anode and of hydrogen at the cathode is a process which takes place of its own accord; hence the gain of free energy due to the conversion of metallic manganese into ions cannot be less than the loss due to the decomposition of water. Following this out quantitatively, it appears that the manganese must dissolve primarily in the form of trivalent ions, which then react with hydroxyl ions, thus:



Increasing the alkalinity of the electrolyte leads to the formation of manganese ions of higher valency in increasing quantity.

A chromium anode in solutions of potassium chloride dissolves with different valencies between 2 and 6. At low temperatures and small

current densities the valency approaches 6; at higher temperatures it falls, but the author could not find any set of conditions in which only one kind of ion is formed. This was equally the case in alcoholic solutions of zinc chloride.

In 16*N*-solutions of potassium hydroxide a tantalum anode is converted into the pentoxide, the electro-chemical valency being 5. The pentoxide forms a layer on the anode which permits a small current to pass. Increasing the applied voltage does not increase this current beyond 0.02 to 0.03 ampere per sq. cm.

T. E.

Migration of Ions in the Water Voltmeter. * FRANZ STREINZ (*Zeitsch. Elektrochem.*, 1916, 16, 744—747).—In Hofmann's voltmeter, in the form commonly used for demonstrating the electrolytic decomposition of water, the sulphuric acid in the cathode tube rises, whilst that in the anode tube falls. The effect is measurable after one hour's electrolysis with 1 ampere or more. The author has compared the rise and fall (due to changes in the density of the acid) in a special apparatus with narrow tubes with those calculated from Hittorf's measurements of the migration of sulphuric acid, and has found a fairly close agreement. The changes of level are, however, larger than those calculated, instead of being smaller, owing to partial equalisation of the densities by diffusion.

T. E.

Electrolysis of the Iodides of the Alkaline Earths Dissolved in Pyridine. GEORG VON ILEVSY (*Zeitsch. Elektrochem.*, 1916, 16, 672—673).—A saturated solution of barium iodide in pyridine contains 20.358 grams per litre at 25°. The conductivity per equivalent at 25° is: $\nu = 9.606$, $\Delta = 8.855$; $\nu = 18.01$, $\Delta = 10.723$; $\nu = 38.59$, $\Delta = 13.045$; $\nu = 81.06$, $\Delta = 15.961$.

When these solutions were electrolysed with platinum electrodes separated by a porous partition, a firmly adherent non-conducting deposit was very soon formed on the cathode. This consisted of barium hydroxide and carbonate, and was due to traces of moisture in the solutions. The pyridine was then dried completely by prolonged electrolysis with 110 volts, but the barium produced by the electrolysis of the dry solutions reacted with the pyridine itself, giving a reddish-brown slime; this was the case even at -40°.

A barium amalgam containing up to 30% of barium may be prepared by electrolysing the dry pyridine solutions with a mercury cathode, the current efficiency being about 80%.

T. E.

Sparking at the Electrodes in the Electrolysis of Molten Salts. ANTON KAILAN (*Zeitsch. anorg. Chem.*, 1916, 68, 141—159).—When molten chlorides are electrolysed with a carbon anode and an iron cathode, the operation is sometimes interrupted by the separation of the mass from the anode, the cessation of the evolution of chlorine, and a rapid fall of the current strength.

It is shown, by measurements of the fall of potential when chlorides are electrolysed, that the effect is not due to the formation of a subchloride, or to the separation of a layer of silica derived from the crucible. The effect is completely inhibited by increase of

temperature, a critical temperature being observed at 500° in a mixture of equal weights of potassium and lithium chlorides, and at about 590° in pure lithium chloride. The addition of lithium bromide hinders the effect. The effect of temperature appears to be connected with the change of viscosity, a conclusion which is confirmed by experiments with dilute sulphuric acid to which glycerol has been added. The effect occurs with a platinum anode as well as with carbon. When the effect is present, the apparent resistance of the cell falls with increasing potential difference. Experiments with an oscillograph show that the variations in the current are very small, provided that the anode dips sufficiently far into the electrolyte. There are about 2000 oscillations in a second. A purely mechanical explanation of the phenomenon is suggested.

C. H. D.

Properties of Salt Solutions in Relation to the Ionic Theory. I. Mol-numbers Derived from the Freezing-point Lowering. ARTHUR A. NOYES and K. G. FALK (*J. Amer. Chem. Soc.*, 1910, 32, 1011—1039).—This paper is devoted to a consideration of the lowering of freezing point caused by acids, bases, and salts, and includes a large number of numerical data collated from the best published observations. The symbol i has been employed to represent the factor by which the number of formula weights, N , associated with 1000 grams of water must be multiplied if the osmotic pressure is to be correctly calculated by the laws of a perfect solution. This has been calculated for several substances in dilute aqueous solution from the simplified equation: $iN = \Delta t / 1.858(1 + 0.0055\Delta t)$, deduced from Washburn's expression (*Tech. Quart.*, 1908, 21, 273); Δt is the lowering of freezing point.

The principal table contains the values of the ratio $\Delta t/N$ (called the formal freezing-point lowering) for forty-two substances, also the weighted mean of several determinations, the best value for the ratio, and finally the mol-number, i , in each case for concentrations between 0.005 and 0.5 equivalent per 1000 grams of water.

The author utilises the results in the discussion of the relation of the mol-number to the type of salt and its variation with concentration.

W. O. W.

Elevation of Boiling Point under Reduced Pressure. KARL DRUCKER (*Zeitsch. physikal. Chem.*, 1910, 74, 612—618).—An apparatus for measuring the elevation of the boiling point under reduced pressure, similar to that used by Rose-Innes (*Trans.*, 1902, 81, 682), is described and figured. As in Beckmann's most recent form of apparatus, electrical heating is used.

The apparatus has been tested with benzene, chloroform, and alcohol as solvents, and camphor as solute with satisfactory results. The observed values of the elevation and those calculated by the van't Hoff formula are in excellent agreement for benzene and for alcohol, but not for chloroform. The experimental value for the latter at 61° is 39.1; in agreement with recent measurements of Beckmann and of Turner (*Trans.*, 1910, 97, 1184), whilst the calculated value at the same temperature is 38.3.

G. S.

Vaporisation in Vacuum. JAROSLAV HLADÍK (*Biochem. Zeitsch.*, 1910, 23, 29—33).—An apparatus is described for the rapid evaporation of solutions under reduced pressure. The vapour is condensed on the inner surface of a cooled bell-shaped vessel, which forms the upper part of the vaporising chamber. The condensed liquid collects in a circular trough which communicates with a collecting bottle outside, through which communication is made with a pump for exhausting the apparatus.

H. M. D.

Binary Solution Equilibria of the Three Isomeric Nitroanilines. ROBERT KREMANN (with J. GEEB and F. NOSS) (*Monatsh.*, 1910, 31, 855—859).—The melting-point curve for mixtures of *o*- and *m*-nitroanilines falls from the melting point of each component to a eutectic point at 47°, the eutectic composition being 66% of *o*-nitroaniline. *m*- and *p*-Nitroanilines give a similar curve, the eutectic temperature being 86°, and eutectic composition 66% of *m*-nitroaniline. Similar results are obtained with mixtures of *o*- and *p*-nitroanilines, the eutectic temperature and composition being 52° and 78% *o*-nitroaniline respectively.

The irregular curves obtained by Tingle and Rolker for these substances (Abstr., 1908, i, 408, 974) are due to the fact that small quantities were used, and the melting points determined by the ordinary method employed in organic chemical practice. T. S. P.

A Simple Distillation Apparatus. F. VOLLRATH (*Chem. Zeit.*, 1910, 34, 1068).—A simple substitute for a condenser is described, consisting of a bottle with double-holed cork, through one hole of which the tube from the distilling flask enters, whilst the other is fitted with a funnel, in which a flask filled with cold water rests.

C. H. D.

Adiabatic Determination of Heats of Solution of Metals in Acids. II. Heat of Dilution of the Acid Solutions. THEODORE W. RICHARDS, ALLEN W. ROWE, and LAURIE L. BURGESS (*J. Amer. Chem. Soc.*, 1910, 32, 1176—1186).—In an earlier paper (this vol., ii, 391) an account was given of a series of determinations of the heat of solution of zinc, aluminium, magnesium, cadmium, and iron in an excess of hydrochloric acid at 20°. In the course of this work, it was found that the heats of dilution, both of the acids and of the residual solutions after the completion of the reactions, affect the results to a considerable extent. In order to reduce to the same standard, it was therefore necessary to carry out experiments on the heats of dilution, and an account of this work is now presented.

The heats of dilution at 25° of the acids $\text{HCl} \cdot 20\text{H}_2\text{O}$ and $\text{HCl} \cdot 8 \cdot 808\text{H}_2\text{O}$ to $\text{HCl} \cdot 200\text{H}_2\text{O}$ were determined, and found to be 0.556 and 1.330 Cal. (or 2.32 and 5.56 kilojoules) respectively. The heats of dilution of the products obtained by dissolving zinc, aluminium, cadmium, and iron in excess of concentrated acid were determined. The substitution of salt for acid was found to affect seriously the heat of dilution, especially in the cases of zinc and cadmium. From these data, the heats of solution of a gram-atom of the five metals in exactly

the theoretical quantity of $\text{HCl} \cdot 200\text{H}_2\text{O}$ have been calculated, and are given in 18° Cals. and also in kilojoules: zinc, 36.6 Cal. or 153.1 kilojoules; aluminium, 127.0 Cal. or 531.0 kilojoules; magnesium, 110.2 Cal. or 460.6 kilojoules; cadmium, 17.2 Cal. or 71.9 kilojoules; and iron, 20.8 Cal. or 87.0 kilojoules. E. G.

Effect of the Glass Surface in Vapour Density Determinations. KARL DRUCKER and G. ULLMAN (*Zeitsch. physikal. Chem.*, 1910, 74, 567—611).—The densities of the vapours of a number of organic compounds at varying temperatures and pressures have been investigated by a modification of the Hofmann method under such conditions that the influence of the glass surface could be determined. The glass surface was varied by using different quantities of glass wool in the interior of the density bulb. The method of measurement adopted is described in detail. The corresponding measurements of Ramsay and Steele (Abstr., 1903, ii, 635) are affected by a considerable error, owing to inaccurate determination of the temperature of the mercury column in the measuring tube.

From the results, the percentage values of pv as compared with that for an ideal gas are calculated and plotted as ordinates against the corresponding pressures as abscissæ. The vapours of benzene, ethyl ether, chloroform, and ethyl alcohol are adsorbed to a small extent on the glass surface, but the adsorption can be neglected for ordinary measurements. Acetic acid, on the other hand, is condensed very considerably; this adsorption is not satisfactorily represented by the ordinary adsorption formula with coefficient less than unity. From the results, the complex constant $k = [\text{bimolecular acid}]/[\text{unimolecular acid}]^2$ has been obtained. At 110°, 95.5°, and 80.2° the values of k are 0.11, 0.25, and 0.60×10^3 respectively. The alteration with temperature is much smaller than that observed by Ramsay and Steele.

Ramsay and Young state that the saturated vapour of acetic acid shows a minimum in the density with change of temperature, but the authors point out that the extrapolation of Ramsay and Young leads to inaccurate values, owing to the influence of adsorption, and that there is no real abnormality of the nature indicated.

The thickness of the layer of acetic acid on the surface of the measuring tube is 0.16—0.60 μ , that of chloroform 0.10—0.20 μ , and that of alcohol only 0.004—0.011 μ . G. S.

van Laar's Theory of the Contraction in Water-Alcohol Solutions. A. G. DOROSHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 442—452. Compare van Laar, Abstr., 1900, ii, 189).—A theoretical discussion of van Laar's theory of the association of liquid molecules, in which the authors conclude that van Laar has given no proof of the fundamental principles underlying his theory. Using van Laar's formula for mixtures of water with propyl and isopropyl alcohols, the contraction of volume of the water, which, according to van Laar, should equal 8.44 at 15.56°, is only 4.67 for the former and 4.79 for the latter; on the other hand, the contraction with ethyl alcohol at 20° is 8.31. Z. K.

Molecular Volumes of Solids. H. H. STEPHENSON (*Chem. News*, 1910, 102, 178—180, 187—189).—Regularity may be traced in the molecular volumes of solids without departing from the atomic volumes of the free elements. Molecular condensation is defined, and shown to be equal for anhydrous salts in each group or sub-group of the Periodic Table for each class of compound, but to vary with the groups and with the acid radicle. The density and molecular volume of any solid compound may, therefore, be calculated if the group condensation is known. The atomic volumes of elements may also be obtained from the density of any of their compounds; for instance, ytterbium has an unknown atomic volume, but its oxide, Yb_2O_3 , has a molecular volume of 43, and the condensation of the sesquioxides of its group is 48, which gives $\text{Yb} = 19.8$, showing a density of 8.7. Hydrated salts, double salts, acid and basic salts, are generally additive in molecular volume, the value for each molecule of water averaging 14. Formulae are given connecting the densities of hydrated and anhydrous salts. It is also shown that the apparent equality of volume of some series of similar and isomorphous salts is due to the fact that they have undergone equal condensation from approximately equal theoretical volumes.

W. P. S.

The Equation of Continuity of the Liquid and Gaseous States of Matter. RICHARD D. KLEEMAN (*Phil. Mag.*, 1910, [v], 20, 665—689).—A mathematical paper in which the expression deduced previously for the attraction between two molecules is made the starting point for the deduction of equations relating to the continuity of the liquid and gaseous states of aggregation. Certain of these relationships are examined by reference to experimental data for various organic compounds.

H. M. D.

Surface Energy and Surface Tension. JAMES E. MILLS and DUNCAN MACRAE (*J. Amer. Chem. Soc.*, 1910, 32, 1162—1176).—Whittaker (Abstr., 1908, ii, 817) has stated that the surface energy of a liquid in contact with its own vapour at any temperature is proportional to the product of the internal latent heat and the absolute temperature. This relation has now been investigated, and found to be only approximately true. It is shown that the relation suggests a division of the so-called surface energy of a liquid into two parts, one due to the liquid surface and the other to the surface of the vapour over the liquid, and this point will be further investigated.

E. G.

Measurement of Surface Tension by the Method of Maximum Pressure of Small Bubbles. R. MAGINI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 184—189).—By the adoption of certain improvements in the experimental arrangements, the author has succeeded in obtaining by this method (compare Cantor, *Ann. Phys. Chem.*, 1892, [ii], 47, 399, 422; Feustel, *Ann. Physik*, 1905, [iv], 16, 61) measurements of the surface tension of benzene, nitrobenzene,

liquid air, and water, with a degree of exactness comparable with that obtained by Rayleigh's wave method (compare Abstr., 1907, ii, 334).

R. V. S.

Surface Tension of Aqueous Solutions and Laplace's Constant. WILLIAM C. McC. LEWIS (*Zeitsch. physikal. Chem.*, 1910, 74, 619—640).—It has already been shown that whilst inorganic salts increase the surface-tension liquid/vapour, they diminish the surface-tension liquid/liquid. In this connexion the surface-tension liquid/vapour has been measured by the dropping method for rosaniline hydrochloride, Congo-red, methyl-orange, methyl-violet, sodium glycocholate, carbamide, malonic acid, and copper sulphate at 14°, 43°, 61°, and 78°. The action of the dissolved substances diminishes gradually as the temperature rises, but in no case has an inversion been observed.

The different effect of inorganic salts in the two cases is discussed and accounted for on the basis of Laplace's theory of internal pressure. Employing instead of the surface-tension, σ , Laplace's capillary factor H_0 , where $\sigma = H_0 \rho^2/2$, ρ being the density, it is shown that H_0 for water is diminished by the addition of all dissolved substances, both at the surface liquid/liquid and at the surface liquid/vapour. With reference to the specific internal pressure K_0 (where $K = K_0 \rho^2$), it is shown that with the exception of those liquids which are completely miscible with water, the addition of any dissolved substance to water diminishes the value of K_0 , whereas, according to Tammann, in the same circumstances, K always increases.

Considering only the surface liquid-vapour, it is shown that the changes of the internal pressure, K , and the surface tension, σ , are always in the same direction. This rule does not apply when the solute is volatile or for certain colloidal solutions.

The considerable diminution of the surface tension produced by certain solutes can be accounted for on the basis of Laplace's theory.

G. S.

The Physico-chemical Theory of Soap Emulsions. Emulsification of Hydrocarbon Oils by Aqueous Solutions of Salts of the Fatty Acids. FREDERICK G. DONNAN and H. E. POTTS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 208—214).—The influence of the sodium salts of eleven normal fatty acids on the surface tension at the contact surface between water and a nearly acid-free hydrocarbon oil has been investigated. The fatty acids used formed a continuous series from acetic to decolic, and, in addition, lauric and myristic acids were examined. All these salts diminish the surface tension, and the extent of the diminution increases in general with increasing molecular weight of the acid. The action begins to be considerable in the case of sodium octoate, and from this point onwards the influence increases more and more rapidly as the molecular weight increases. In harmony with these observations, it is found that the sodium salts of lauric and myristic acids are the only members of the series which give rise to emulsification effects. In these two cases the emulsification capacity increases rapidly with the concentration of the dissolved salt, and then decreases rapidly at higher concentrations. The existence of this

maximum effect is attributed to the salting-out action of the sodium ions. It is supposed that the changes in surface tension, which are obviously connected with the emulsifying power of certain solutions, are accompanied by changes in the potential differences at the contact surface.

H. M. D.

Autosorption (Auto-adsorption). WILLIAM C. McC. LEWIS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 197—205).—The views expressed in this paper relating to the nature of the liquid vapour contact surface have been for the most part published previously (compare this vol., ii, 829). The term autosorption is introduced in reference to the greater density of the surface layer of a liquid as compared with its bulk density. Whereas autosorption has been found for a number of liquid organic compounds which have been examined, there appears to be little difference in the surface and bulk densities in the case of the elements mercury, bromine, and iodine. For these substances the autosorption is therefore of very small magnitude, and this appears to be the case for zinc and cadmium.

The surface and bulk densities of water are employed to calculate the difference between the quantity of water actually present in the surface layer of water and that which would be present if capillary forces were eliminated. The value thus obtained is of the order 10^{-6} — 10^{-7} gram per sq. cm.

H. M. D.

Changes in Tanning [Processes]. REGINALD O. HERZOG and GEORG ROSENBERG (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 222—227).—In continuation of previous experiments (*Abstr.*, 1908, ii, 262) on the adsorption of substances from aqueous solution by lightly chromed hide powder, the authors have made similar measurements with non-chromed powder. Aqueous solutions of sodium picrate, silver nitrate, crystal-violet, patent-blue, new-magenta, and phenol were examined. The removal of sodium picrate from aqueous solution takes place in accordance with the simple law of distribution, the value of the exponent in the adsorption formula being equal to unity. With chromed hide powder the proportion of adsorbed substance increases somewhat with the concentration of the solution. In the case of silver nitrate, the data agree with the formula $K = B^m/C$, in which C is the quantity of the adsorbed substance, and B is the concentration of the residual solution, if m is made equal to 0.5. The adsorption of the three colouring matters is also in accord with the exponential equation, but the data for phenol show considerable divergence, and this is considered to indicate that the removal of phenol by the hide powder is not due to a simple adsorption process. An empirical formula is given by means of which the data for phenol can be satisfactorily reproduced.

In general, there is no essential difference in the behaviour of chromed and non-chromed hide powder in regard to their adsorptive properties.

H. M. D.

The Capillary Rise of Acids. ZDENKO H. SKRAUP, E. KRAUSE, and A. VON BIEHLER (*Monatsh.*, 1910, 31, 753—776).—In the case of all organic acids, the regularities which have been previously observed

are confirmed (compare Ahstr., 1909, ii, 868; this vol., ii, 191). The stronger the acid is, the more it is absorbed by the filter paper, and the less is the capillary rise; the weaker it is, the less is the absorption. The large capillary rise with acetic acid is much diminished when it is transformed into trichloroacetic acid; the same result is true for the pairs of acids: succinic and dibromosuccinic; benzoic and nitrobenzoic.

Phosphoric acid has a very small capillary rise, and the suggestion has been made that this is due to its polybasicity. In order to test the validity of this suggestion, measurements have been made with benzene-mono-, di- and tri-sulphonic acids, with different carboxy-acids of benzene, including mellitic acid, and with oxalic, malonic, succinic, glutaric, and tricarballylic acids. It is found that a decrease in the capillary rise does not take place with increase in the basicity of the benzenesulphonic acids; it does take place with the carboxy-acids of benzene, but the decrease stops when the value of the capillary rise becomes the same as that for strong acids. In the case of tricarballylic acid, the capillary rise is greater than that for malonic, succinic, or glutaric acids.

Arsenic acid is similar to phosphoric acid, in that it has an abnormally low capillary rise. Pyrophosphoric acid, in contradistinction to orthophosphoric acid, shows an abnormally high rise, whereas metaphosphoric and phosphorous acids give much lower rises, the rise with the latter acid approximating to that for relatively strong acids. Hydrofluoric acid gives practically the same result as hydrochloric acid, although it is much less dissociated.

Using a modification of Holmgren's circle method, the absorptions of sulphurous and hydrocyanic acids and solution of hydrogen sulphide have been investigated. Hydrocyanic acid has a higher capillary rise than hydrochloric acid, whereas with the other two acids the rises are practically the same as for hydrochloric acid.

The present investigation shows that there are undoubted regularities in the case of organic acids, but with inorganic acids the number of irregularities has been increased.

T. S. P.

Osmotic Equilibrium between Two Fluid Phases. L. GAY (*Compt. rend.*, 1910, 151, 612—616).—A purely mathematical treatment of the subject.

W. O. W.

Relation of Osmotic Pressure to the Intrinsic Pressure of Liquids. M. M. GARVER (*J. Physical Chem.*, 1910, 14, 651—664. Compare this vol., ii, 398).—The intrinsic or internal pressure of a gas in which the molecules exercise no attraction for one another is numerically equal to the extrinsic pressure exercised by the gas on the containing vessel. The intrinsic pressure of a liquid is equal to the extrinsic pressure plus the effect of molecular attractions, and has a different value in the surface film where molecular attractions are not wholly balanced.

The author assumes that the average molecular energy of translation is the same in the gaseous and liquid phases if the molecular

weight (m) is the same, since the mean square of the molecular velocity (v) in either phase represents the absolute temperature.

If p_1 and P_1 are the intrinsic pressures of gas and liquid respectively, $P_1 = \frac{2}{3}(n_1 m v^2)/2 = \frac{2}{3}(n_1 m v^2)/2 \times n_2/n_1 = p_1 \times n_2/n_1$, where n_2 and n_1 are the numbers of molecules per unit volume in liquid and vapour phase respectively. The intrinsic pressure of a liquid is very simply obtained by multiplying the vapour pressure by the ratio of densities of liquid to vapour. Further, it is deduced that $PV = pv = RT$, that is, the gas laws hold for liquids if P is interpreted as intrinsic pressure. If P_1 and P_2 be the intrinsic pressures of a solvent and solution respectively, $P_1 - P_2 = \rho RT \log p_1/p_2$ = the osmotic pressure, where p_1 and p_2 are the vapour pressures of solvent and solution respectively. Osmotic pressure is thus defined as the reduction in intrinsic pressure or normal activity of the solvent due to the introduction of the solute. This reduction is brought about by the reduction of the number of molecules of solvent from N to $(N - n)$, n being the solute molecules. The volume concerned in osmotic calculations is the volume of the solvent multiplied by N/n , whilst the pressure is diminished in the ratio n/N .

The intrinsic pressure of water at 0° is 1235 atm. A weight-normal solution contains 1 molecule of solute to 55.6 of solvent, and its osmotic pressure is therefore $1235/55.6 = 22.2$ atm.

If the membrane is not wetted by the liquid, a surface film exists, which with its unbalanced molecular attractions prevents free circulation of the solvent so that no osmosis occurs. The principal part in osmotic phenomena is played by the solvent, and some form of association hypothesis is necessary.

R. J. C.

Methods of Diffusion Experiments. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 219—222).—The nature of the precipitation membranes which are formed when gelatin solutions of silver nitrate and the halogen salts of the alkali metals are juxtaposed is shown to depend on the circumstances in which the diffusion processes take place.

H. M. D.

Inconstancy of the Solubility Product. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1910, 32, 1186—1193).—Cameron (Abstr., 1902, ii, 75) has found that the solubility of gypsum is increased by addition of sodium chloride up to a certain concentration, and beyond this point the solubility diminishes. Hill and Simmons (Abstr., 1909, ii, 647) have observed a similar behaviour when silver sulphate is treated with nitric acid solutions. It is shown that this decrease in total solubility can only be accounted for by assuming that the concentrations of the ions of the solute have diminished, and that the value of the solubility product has accordingly been reduced. The work now described was carried out with the object of gaining further evidence on this point.

The solubility of thallous chloride in acetic acid of concentrations between zero and $16N$, and that of tetramethylammonium iodide in potassium hydroxide of concentrations between zero and $8.3N$, has been determined at 25° . Measurements of the conductivity of a

saturated solution of tetramethylammonium iodide and of solutions varying from $N/8$ to $N/1024$ have also been made for use in the calculations. The results show that the solubility of thallous chloride and tetramethylammonium iodide is so diminished in presence of the other electrolytes as to prove conclusively that the solubility product is not a constant, but that it decreases with increase in the total concentration of electrolytes present.

E. G.

Ionisation Relations of Sulphuric Acid. ARTHUR A. NOYES and M. A. STEWART (*J. Amer. Chem. Soc.*, 1910, 32, 1133—1162).—Sulphuric acid is usually assumed to undergo ionisation in aqueous solution according to the equations: $H_2SO_4 = H^+ + HSO_4^-$ and $HSO_4^- = H^+ + SO_4^{2-}$, but the only investigation yielding valuable evidence as to the proportion of the HSO_4^- ion present is that of Noyes and Eastman (*Carnegie Inst. Publications*, 1907, 63, 239). The present work was therefore undertaken with the view of obtaining more definite information with regard to the ionisation of this acid.

The hydrogen-ion concentration, C_H , can be calculated from the value of the mol. number, i , as determined from the depression of the f. p., by means of the relation $C_H/C = i - 1$. The values of C_H/C at 0° have been thus derived from the recorded f. p. data.

It is shown that by combining conductivity and transference data, there can be derived maximum and minimum values of the hydrogen-ion concentration in sulphuric acid corresponding with the two limiting cases in which the only negative ion present is SO_4^{2-} or HSO_4^- , and in this way limiting values of C_H/C at 25° and 0° have been calculated. Incidentally it has been found from a study of existing conductivity data at 0° that the best values for the equivalent conductivity at 0° of certain ions are $\Lambda_K = 40.3$, $\Lambda_{Cl} = 41.1$, $\Lambda_{SO} = 42.8$, and $\Lambda_H = 224$.

The value of Λ_{HSO_4} at 25° and 0° can be approximately calculated from the transference and conductivity data, if it is true that the HSO_4^- ion is present in the sulphuric acid solution in considerable quantity so that its conductivity may enter as a factor. The values obtained are 35—40 at 25° , which are nearly half of that of Λ_{SO} , namely, 79 at 25° .

The values of C_H/C have also been calculated from a consideration of the relative effects of sulphuric and hydrochloric acids on the hydrolysis of sucrose at 25° as determined by Ostwald (*Abstr.*, 1885, 882), and on that of ethyl acetate as determined by Kay (*Proc. Roy. Soc. Edin.*, 1898, 22, 493).

A new isohydric method of determining the hydrogen-ion concentration is described, which consists in determining the relative concentrations of hydrochloric and sulphuric acids which drive back the ionisation of picric acid to the same extent.

The values of C_H/C at various concentrations at 0° and 25° obtained by these different methods are tabulated. In order to derive the concentrations of the HSO_4^- and SO_4^{2-} ions from the values of the hydrogen-ion concentration, Noyes and Eastman (*loc. cit.*) assumed that under corresponding conditions the first hydrogen of sulphuric acid is dissociated to an equal extent to that of hydrochloric acid, and

hence estimated the concentration of the non-ionised sulphuric acid. From this concentration and that of the hydrogen ion, the concentrations of the SO_4 and HSO_4 ions were obtained by subtraction. Similar calculations have now been made, and the results show that both the SO_4 and HSO_4 ions are present in large proportions at medium concentrations, that the latter is present in much larger quantity at 0.05 formal and the former at 0.005 formal, and that at 0.05 formal the ratio $\text{CHSO}_4/\text{CSO}_4$ increases greatly between 0° and 25° . The hydrogen-ion concentration decreases markedly within the same range of temperature.

Experiments have been made on the distribution of sulphuric acid between water and amyl alcohol. The ratio of the concentration of the acid in the alcohol to that in the water was found to increase as the proportion of non-ionised sulphuric acid in the aqueous solution increased. The ratio of this increase is somewhat smaller even than in the case of hydrochloric acid, indicating that the non-ionised sulphuric acid is formed from two ions, H^+ and HSO_4^- , instead of from three ions, H^+ , H^+ , and SO_4^{2-} .

Determinations have been made of the transference of Na, H, and SO_4 during the electrolysis of sodium hydrogen sulphate at 25° . The conductivity of this salt has also been measured at various concentrations at 25° . By combining these data, the concentrations of Na and H ions in a 0.1 formal solution have been calculated, and the values $C_{\text{Na}}/C = 0.68$ and $C_{\text{H}}/C = 0.44$ obtained.

From the results obtained by Kay (*loc. cit.*) on the catalysis of ethyl acetate by 0.1 formal sodium hydrogen sulphate, the value of C_{H}/C has been derived and found to be 0.416.

By means of the values of C_{H}/C and $C_{\text{H}}/C_{\text{Na}}$ derived from the transference and conductivity data, the concentrations of the other ions in a 0.1 formal solution of sodium hydrogen sulphate have been computed, and found to be $C_{\text{HSO}_4}/C = 0.44$ and $C_{\text{SO}_4}/C = 0.34$ respectively.

From these data, and also from the corresponding data for 0.05 formal sulphuric acid, the values of the product $C_{\text{H}}\text{CSO}_4/\text{CHSO}_4$, the ionisation constant of the second hydrogen of the acid, have been found to be 0.034 and 0.031 respectively. E. G.

Hydrolysis of Cyanogen. R. NAUMANN (*Zeitsch. Elektrochem.*, 1910, 16, 772—778).—The conductivity of potassium cyanate solutions is measured; the mobility of the cyanate ion at 18° is 56.5. When cyanogen is passed into aqueous solutions of potassium hydroxide, the conductivity diminishes to a constant value. The observed conductivity agrees well with that calculated on the assumption that cyanide and cyanate are the only products. The conductivity of solutions of cyanic acid at 0° is measured, and the dissociation constant found to be about 120×10^{-6} . When cyanogen is passed through water at 0° , the conductivity increases to a constant value, owing to the formation of cyanic acid (the hydrocyanic acid is practically a non-conductor); the saturated solution contains 0.221 gram-molecule of cyanogen and 0.00005 gram-molecule of cyanic acid per litre, so that 0.023% of the cyanogen is hydrolysed. At the ordinary temperature, the conductivity

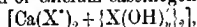
of water through which cyanogen is passing depends very much on the rate of the current of gas, and it diminishes rapidly when the gas is stopped. This is due to the decomposition of the cyanic acid into ammonia and carbon dioxide. Cyanogen has, therefore, no definite solubility in water at 18°, the quantity absorbed increasing continuously with the time of contact.

In the calculation of the dissociation constant of hydrocyanic acid (this vol., ii, 386) a serious error was made, the correct value is $\log_{10} K = -29.13$ instead of -10.14 . This new value is not in harmony with the view that the *E.M.F.* of the hydrogen-cyanogen element is due to the formation of hydrocyanic acid.

• T. E.

Electrochemistry of Proteins. II. Dissociation of Basic Caseinogenates of the Alkaline Earths. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, 14, 601—611. Compare this vol., ii, 679).—It is probable, since the neutral and basic caseinogenates of the alkalis obey Ostwald's dilution law, that a molecule of caseinogenate gives only two ions. The cation is supposed to be a complex ion containing the metal in a non-dissociable form. On this hypothesis basic calcium, strontium, and barium caseinogenates, instead of dissociation into three ions, one of which would be the metal, should give only two complex ions, and the dissociation should obey Ostwald's law.

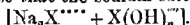
The solutions examined contained 1 gram of caseinogen to 80×10^{-5} gram-equivalents of calcium, strontium, and barium hydroxide; they were practically neutral to phenolphthalein. The conductivity-dilution curve is in accord with Ostwald's law for a binary electrolyte. If v_1 and v_2 are the ionic velocities and ρ the number of molecules of caseinogenate formed from one molecule of base, the values of $\rho(v_1 + v_2)$ are about twice as great for the caseinogenates of the alkalis as for the alkaline earths. As all the ions concerned are supposed to be complex protein ions, $\rho(v_1 + v_2)$ must be much the same in all the salts. Hence ρ may be taken as two for the alkalis, and one for the alkaline earths. The simplest formula of sodium caseinogenate is $[\text{NaX}'' + \text{X(OH)}_n]'$, and of calcium caseinogenate,



each ion having twice as many charges as there are molecules of base per molecule of caseinogen.

The values of $(v_1 + v_2)$ are about 40×10^{-5} at 30°. This is approximately the value calculated by Bredig as the minimum which ionic mobility approaches when the ions become very large. The caseinogenates of the alkalis are nearly completely dissociated, whilst calcium caseinogenate is only 57% dissociated.

The freezing-point determinations of Robertson and Barnett (*Abstr.*, 1909, i, 447) are explainable on the hypothesis that caseinogenate ions are quadrivalent, so that the sodium salt is written:



This formula suggests that two CO_2H groups of the caseinogen molecule are active in the neutralisation of bases.

R. J. C.

Influence of the Degree of Dispersity of a Solid Crystal on its Melting Point. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 205—208).—A theoretical paper in which the author analyses

the relationships involved in the transition from the liquid to the amorphous and crystalline solid states of aggregation. H. M. D.

A General Theory for Obtaining Disperse Systems by the Dispersion Method. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 453—474. Compare Abstr. 1909, ii, 132, 221, 306, 606, 646).—A more detailed theoretical discussion of matter already published, and a classification of the methods of peptization. All the dispersion methods of obtaining disperse systems can be explained according to one general theory, the fundamental general principle of which can be formulated thus: If for some reason or other the intensity of the forces of solution at the surface of disperse particles increases to an extent not greater than that at which the velocity of recrystallisation becomes considerable, then the disperse particles are peptised by the dispersion medium. For an explanation of the theory, the paper itself must be consulted. Z. K.

Colloidal Chemistry. A General Introduction. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 476—480).—A short historical and theoretical introduction to the two following papers. A good general method of obtaining any solid substance in the state of an amorphous solid solution of any degree of dispersion has been devised, and is based on the rapid cooling of a dilute liquid solution of a substance in a dispersion medium, which, in the pure state itself, solidifies to a glass when rapidly cooled.

The best method of obtaining liquid colloidal solutions is based on the rapid condensation of the molecules of the dissolved substance, when the solvent is replaced by a dispersion medium which dissolves the solvent, but, practically, does not dissolve the dissolved substance. If a concentrated solution is added to such a dispersion medium, fine disperse precipitates are obtained, but not colloidal solutions. Z. K.

A Simple General Method for Obtaining Solid Colloidal Solutions of any Degree of Dispersion. P. P. VON WEIMARN and J. B. KAGAN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 480—484. Compare preceding abstract).—When a transparent solid solution is heated gradually, the viscosity of the dispersion medium decreases, whilst the velocity of the molecules and molecular aggregates and the coefficient of diffusion increases; consequently, at first, when L in the formula $W = K(Q - L)/L$ (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 214—228) has not yet increased appreciably, the condensation process occurs, and a bluish-violet opalescence appears, which becomes more and more marked until the solution becomes turbid. When L has increased sufficiently, the dispersion process commences, which is indicated by a diminution in the turbidity of the solution, and by a gradual re-appearance of the bluish-violet opalescence, which then gradually disappears.

When a 0.04% solution of sulphur in alcohol is immersed in liquid air, a solid, strongly opalescent, but partially transparent suspended solution is obtained, which, when heated and well shaken, only shows

the second, the dispersion, process described above. With a 0.02% solution of sulphur a wholly transparent solid solution is obtained, which behaves entirely in accordance with the above theoretical scheme. The solution can be fixed or arrested at any stage of opalescence, or at any degree of dispersion, by rapidly immersing the tube containing the solution at the given stage in liquid air. By employing very dilute solution of sulphur, molecular dispersed solid solutions are obtained, in which, when heated, the condensation process is so rapidly followed by the dispersion process that opalescence can sometimes scarcely be observed. Exactly similar results were obtained with phosphorus, sodium bromide, and sodium and potassium chlorides.

A 0.25% solution of phosphorus in alcohol gives a turbid glass; 0.05–0.04% solution yields a partly transparent suspended solid solution, whilst 0.025% gives a wholly transparent suspended solid solution.

Z. K.

A Simple Method of Obtaining Sulphur, Selenium, Tellurium, and Phosphorus in a Colloidal State. P. P. von WEIMARN and B. V. MALJISHEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 481–487. Compare two preceding abstracts).—Five to twenty-five c.c. of a solution of the metal, saturated at the ordinary temperature or at the boiling point of the solvent (alcohol for sulphur and phosphorus, carbon disulphide for selenium), are rapidly added to 1000 c.c. of the dispersion medium and stirred vigorously. The dispersion medium for sulphur and phosphorus was cold water; for selenium, cold ether. The concentrations of these suspended solutions varied within the limits of several 1/10,000's to several 1/100's, the solutions in the latter case being very turbid and rapidly coagulating.

The solid solutions are coloured, opalescent, and fairly stable, the stability of the phosphorus and selenium solutions depending on the peptisation processes.

This method of obtaining colloidal solutions is recommended for lecture experiments. The probable solubility of selenium in carbon disulphide is 0.02–0.015 gram in 100 of solvent.

Colloidal tellurium is obtained by adding 0.1 of the element to 5 c.c. of a boiling solution of potassium hydroxide, saturated at the ordinary temperature, and adding the solution of the metal thus formed to 1000 c.c. of cold water, the mixture being stirred vigorously. The stability of the colloidal tellurium solution depends directly on the peptisation processes, and can be greatly increased. The solution can also be made more stable by the addition of gelatin or similar substances.

Z. K.

Phenomena of the Colloidal State. PAUL ROHLAND (*Biochem. Zeitsch.*, 1910, 28, 53–55).—Observations relating to the behaviour of adsorbed substances are referred to as showing that substances in the colloidal condition are frequently much less reactive than they are in the crystalloidal form. The viscosity of colloidal substances is very often increased or decreased by special types of ions.

H. M. D.

The Purification of Colloids by Dialysis. RICHARD ZEIGMOND and R. HEYER (*Zeitsch. anorg. Chem.*, 1910, 68, 169—187).—A comparison of parchment, collodion, and fish-bladder membranes in the dialysis of colloidal silica, shows that the last-named acts most rapidly. Collodion membranes, which are perfectly impervious to colloidal silver, allow silica to pass with considerable ease. Continuous renewal of the water in the outer vessel has no advantage over a renewal every two hours. With a suitable membrane, the chlorine is reduced to the limit of recognition by means of silver nitrate in about twenty hours.

An improved dialyser is described, in which a membrane is stretched over a vulcanite ring, placed on a vulcanite tray with edges only 4 mm. high, and provided with radial ribs. The water enters at the centre of this tray, and travels radially in a thin sheet, escaping at the circumference. This appliance allows of rapid dialysis.

In order to estimate chlorine in colloidal solutions of silica, the free hydrochloric acid is first estimated by titration with $N/100$ -sodium hydroxide. Another quantity is then exactly neutralised with sodium hydroxide, a drop of 5% potassium chromate solution is added, and the chlorine is titrated with $N/100$ -silver nitrate. A standard solution may be used for comparison. Under these conditions, 0.01 c.c. of $N/100$ -silver nitrate, run in from a graduated capillary pipette, produces a distinct change of colour, and it is possible to detect 0.004 mg. of chlorine in 1 c.c. of the dialysed liquid. The dialysis, however, proceeds beyond this limit, and it is necessary to employ JORDIS' method (this vol., ii, 416) of distillation with sulphuric acid. The residue obtained after neutralising 100 c.c. and evaporating to dryness is transferred to a small distilling flask, 0.5 to 1 c.c. of concentrated sulphuric acid is added after closing the apparatus, and the distillation is continued until nearly all the sulphuric acid has passed over. The chlorine in the absorbing liquid is estimated by RICHARDS' nephelometric method (Abstr., 1904, ii, 287) by means of silver nitrate.

The precipitation of silver chloride is not hindered by the presence of colloidal silica, unless the latter is in very large excess. If some sulphuric acid is present, the precipitation is in all cases normal.

Sodium sulphate is much less readily removed from silica by dialysis than chlorides. Alumina and iron, derived from the sodium silicate used, are not eliminated. Minute quantities of hydrochloric acid increase the stability of the colloid, sodium hydroxide at first diminishes it, but subsequent additions increase the stability.

C. H. D.

The Binary System Pyridine-Potassium Thiocyanate. KARL L. WAGNER and ERNST ZERNER (*Monatsh.*, 1910, 31, 833—841).—The course of the fusion and solubility curves of two substances between the melting and eutectic points has been thoroughly studied only for the case that the mutual solubilities of the two substances decrease with falling temperature. The temperature-concentration diagram for fusions containing the two substances is then the ordinary curve with two branches, neither of which shows a minimum, and one eutectic point. When the solubility of one substance in the other passes through

a minimum there are four cases which are theoretically possible, and for which the authors give the curves. One of these is where the two branches of the fusion curve intersect below the minimum in an eutectic point. The system pyridine-potassium thiocyanate partly conforms to this type, differing from it in that between the eutectic point and the melting point of the potassium thiocyanate there is a four-phase invariant system, namely, liquid pyridine-liquid potassium thiocyanate-solid potassium thiocyanate-vapour. The mutual solubility of the two liquid phases increases as the temperature falls.

The various points on the curves were obtained by heating together weighed quantities of pyridine and potassium thiocyanate in sealed tubes, and observing the temperature at which the crystals disappear or are deposited.

The eutectic temperature is approximately -43.3° , the mixture containing 3.1% of potassium thiocyanate. The four-phase system is formed at 188.5° .

Potassium thiocyanate has m. p. 173.8° .

T. S. P.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IV. Phenol and the Methylcarbamides. ROBERT KREMANN [with J. DAIMER, F. GUGL, and H. LIEB] (*Monatsh.*, 1910, 31, 843-853. Compare Abstr., 1907, i, 912).—The melting-point curve for mixtures of phenol and *o*-dimethylcarbamide falls from the melting point of the dimethylcarbamide to a break at $25-25.5^{\circ}$, and then to a eutectic point at 9° , representing mixtures containing 63% and 84% of phenol respectively. The break at 25° is due to the separation of the compound formed from one molecule of each of the components, the composition of the compound being determined by measuring the times of arrest for mixtures varying in composition from 0-63% phenol. The eutectic is a mixture of this compound with phenol.

The curve obtained for mixtures of phenol and monomethylcarbamide is similar in character, the break occurring at 8° and the eutectic at -7° representing mixtures containing 60% and 77% of phenol respectively. The break at 8° is again due to the separation of a compound containing one molecule of each of the components.

The curve for mixtures of phenol and *s*-dimethylcarbamide is the ordinary one for a two-component system giving one compound and two eutectics. The compound is formed from two molecules of phenol and one molecule of dimethylcarbamide, and has m. p. 14° . The eutectic temperatures are $+5^{\circ}$ and -3° , representing mixtures containing 81% and 47% of phenol respectively.

The above results support the statement that asymmetric substitution diminishes the power to form compounds, whereas symmetrical substitution does not have this effect (compare Abstr., 1906, ii, 268).

T. S. P.

Equilibrium between Solid Cuprous Iodide and Aqueous Solutions Containing Cupric Salt and Iodine. WILLIAM C. BRAY and G. M. J. MACKEY (*J. Amer. Chem. Soc.*, 1910, 32, 1207-1214).—The results described in this paper are the outcome of a study of the law of the mass-action in dilute aqueous solutions.

Cuprous iodide is only slightly soluble in water, but in the presence of iodine a considerable amount dissolves, owing to the formation of cupric iodide and tri-iodide. The following equilibria are involved: $\text{CuI(solid)} + \frac{1}{2}\text{I}_2 = \text{Cu}^{++} + 2\text{I}^-$ and $\text{I}_2 = \text{I}_3 + \text{I}^-$.

Values have been determined at 25° under widely different concentrations for the former equilibrium. The ionic concentrations in the various mixtures were calculated by means of the relations derived from conductivity measurements. The values obtained for the equilibrium function $K' = (\text{Cu}^{++})(\text{I}^-)^2/\text{I}_2$ show that this equilibrium conforms with the law of mass-action only as far as the influence of iodine is concerned and deviates from it when cupric salt, iodide, or other salt is added. In all cases, however, the deviations are of such a nature that K' increases with increasing concentration. This result is an illustration of the rule that when the concentration of an ion is based on conductivity measurements, the ratio of its "activity" (Lewis, *Abstr.*, 1908, ii, 16) to its concentration decreases somewhat with increasing ion concentration. From this rule it follows that the solubility product of a salt will not be constant, but will increase with increasing ion concentration.

Values have also been calculated for the equilibrium function, $K = (\text{I}^-)(\text{I}_2)/(\text{I}_3)$. The results confirm the conclusion (this vol., ii, 820) that K decreases with increasing concentration of iodide, but that other salts do not produce a similar effect.

Conductivity determinations made with several of the equilibrium solutions have shown that cupric iodide and tri-iodide are ionised to the same extent as magnesium chloride, and that cupric nitrate is ionised to a somewhat smaller extent. E. G.

Equilibria in the Precipitation of Metals by Hydrogen Sulphide. LUDWIK BRUNER and J. ZAWADSKI (*Bull. Acad. Sci. Cracow*, 1909, 267—312).—The precipitation of thallium sulphide by hydrogen sulphide is a reversible reaction. Measurements in solutions of different acid and hydrogen sulphide concentrations show that at 25°, $K = [\text{Ti}^{++}][\text{H}_2\text{S}]/[\text{H}^+]^2 = 0.637$. The equilibrium has also been approached from the other side by adding thallium sulphide to sulphuric acid and passing hydrogen sulphide. Measurements at 0° and 40° lead to values for the equilibrium constant from which a value for the heat of precipitation of thallium sulphide is obtained by van't Hoff's equation, in agreement with that derived from thermochemical data.

The values of K obtained for the precipitation of ferrous sulphide vary, owing to experimental difficulties, but lie between 2.7×10^8 and 9.1×10^8 . Calculations are made of the solubility products of iron, cadmium, and lead, and the results of previous observers for these and other sulphides are discussed and criticised. It is shown that the published values for the solubility of sulphides in pure water, calculated from the electrical conductivity, are not in accordance with the analytical behaviour of the metals.

The results from thallium sulphide are employed to calculate the electrolytic potential of sulphur. The experiments with lead sulphide lead to a result in close agreement with this. From the potential thus

obtained, the solubility products of the sulphides are calculated by means of Bodländer's formula, and values are obtained in good agreement with the experimental results, with a few exceptions. The observed solubilities are then used to calculate the heat of formation of the sulphides, in good agreement with Thomsen's results.

C. H. D.

Equilibria in the Precipitation of Metals by Hydrogen Sulphide. LUDWIK BAUNER and J. ZAWADSKI (*Zeitsch. anorg. Chem.*, 1910, 67, 454—455).—Owing to differences in the methods of expressing concentrations in the data from different sources, there are certain numerical errors in the authors' calculations (see preceding abstract). The corrected value for the potential of sulphur against the hydrogen electrode is $E_h = +0.545$. Employing this value to calculate the solubility constants, and adopting more recent values for the electrolytic potentials of iron and silver, the agreement between the calculated and observed values is improved. The imperfect agreement in the case of zinc is attributed to the known transformation of βZnS into the less soluble αZnS .

C. H. D.

Equilibria in the Action of Potassium Hydroxide on Mercuric Bromide and Chloride. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 68, 165—168).—In the reaction: $\text{HgBr}_2 + 2\text{KOH} \rightleftharpoons \text{HgO} + 2\text{KBr} + \text{H}_2\text{O}$, the constant $[\text{HgBr}_2][\text{KOH}]^2/[\text{KBr}]^2$ is found to have the average value 10.1×10^{-4} . Basic salts are, however, also formed. The reaction of potassium bromide with an excess of mercuric oxide (Bersch, Abstr., 1891, 1413; Bugarszky, Abstr., 1893, ii, 450, 566) gives a constant 15×10^{-4} .

The precipitation of mercuric chloride by an excess of potassium hydroxide has also been measured in two concentrations. C. H. D.

Kinetics of the Formation of Ethyl Ether from Alcohol and Ethyl Hydrogen Sulphate. ROBERT KREMANN (*Monatsh.*, 1910, 31, 671—683).—The rate at which the reaction between ethyl alcohol and ethyl hydrogen sulphate proceeds at 100°, 125°, and 135° has been determined by measuring the increase in acidity during the course of the reaction. The increase in acidity is not a direct measure of the extent to which the reaction has taken place, since the sulphuric acid formed enters into reaction with the alcohol to re-form ethyl hydrogen sulphate according to the equilibrium reaction: $\text{EtOH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{EtSO}_3\text{H} + \text{H}_2\text{O}$. At the temperature of experiment this equilibrium adjusts itself practically instantaneously, and since the equilibrium constant has been previously determined (this vol., ii, 700), the correction to be applied to the observed increase in acidity in order to obtain a correct measure of the velocity of reaction can be determined.

The alcohol was always in large excess, and the reaction is assumed to be bimolecular, a number of simplifications having to be made in order to reduce the differential equation to a form in which it can be readily integrated.

The values obtained for the velocity constant are not even approximately constant, but decrease very considerably during the

course of the reaction, the rate of decrease being the greater the greater the initial concentration of the ethyl hydrogen sulphate. This is probably due to the retarding effect of the water formed by the action of the alcohol on the sulphuric acid.

A comparison of the times necessary for the reaction to proceed to the same extent at different temperatures gives a temperature quotient of 2.5 for 10° .

The ordinary method for making ether is discussed in the light of the results obtained.

T. S. P.

The Mechanical Vibration of Atoms. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], 20, 657—660).—On the assumption that the atoms of an element may be replaced by cubes of uniform density, having the same mass as the atoms, and just large enough to circumscribe them, the author calculates the wave-lengths corresponding with the fundamental mechanical vibrations of the atoms of the alkali metals and the halogens. It is shown that the wave-lengths corresponding with the vibration of the molecules of the alkali halogen salts are probably represented by the sums of the wave-lengths of the constituent elements. When the computed wave-lengths for sodium chloride, potassium chloride, bromide and iodide are compared with the lengths of the longest infra-red waves examined by Rubens and Mollnagel in the case of these four substances, it is found that a nearly constant ratio of eight is obtained. According to this, the calculated mechanical period of vibration is only three octaves below the lowest period experimentally investigated in each of these four cases.

H. M. D.

New Proof of the Existence of Molecules. THE SYEDBERG and NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1910, 74, 513—536. Compare Abstr., 1909, ii, 277, 561, 723).—The relationship between the absorption in a colloidal solution and the size of the particles has been further investigated. Some of the measurements were made with a Vierordt spectrophotometer and a light source giving a continuous spectrum, but the later and more accurate measurements were made with a König-Martens spectrophotometer with homogeneous light.

The results are expressed in terms of $k = \frac{1}{d \log_e} \log \frac{I_0}{I}$ or $k_m = k/\text{mol.}$ per litre, where I_0 and I represent the intensities of the light before and after traversing the absorbing layer, and d is the thickness of the absorbing layer in cm.

A series of solutions of colloidal gold containing particles of different magnitude have been prepared, and it is shown that the wave-length for maximum absorption diminishes progressively as the size of the particles diminishes, whilst the maximum value of k_m increases at first, attains a maximum, and finally diminishes with progressive diminution in the size of the particles. When a solution of phosphorus in ether is added to a solution of chlorauric acid, HAuCl_4 (the absorption maximum of which is in the ultra-violet), the absorption spectrum is at first displaced a little towards the ultra-violet, and then a slow continuous displacement towards the visible spectrum occurs. The

change from gold solutions with a known degree of dispersion (size of particle) and absorption in the visible region to chlorauric acid (with molecular dispersion and maximum absorption in the ultra-violet) is continuous.

Examination of solutions of colloidal and dissolved selenium confirms the above results; in this case the maximum absorption of the molecular solution (in carbon disulphide) lies in the visible region. Some observations with iodogotin solutions are also described.

A relationship has been found between the absorption exerted by each particle and the degree of dispersion.

G. S.

Berzelius' Error as to the Discoverer of the Law of Neutralisation. MAX SPETER (*J. pr. Chem.*, 1910, [ii], 397—408).—Historical.

C. S.

A Simplified and Improved Form of Toepler's Mercury Air-Pump. ANDREAS VON ANTROPOFF (*Chem. Zeit.*, 1910, 34, 979).—The throwing up of mercury in the Toepler pump is avoided in this form by placing the cylindrical vessel in an inclined position. The vessel need not have a capacity of more than 100 c.c. It is drawn out into a conical form at its upper end, at the junction with the capillary. The pump may be worked rapidly without injury, and is very simple in construction.

C. H. D.

New Modification of the Kipp Gas Generator. F. ALEX. McDERMOTT (*J. Ind. and Eng. Chem.*, 1909, 1, 811—812).—The paper contains a sketch and description of a modification of the Kipp gas generator, in which the base is made cylindrical with a dome-shaped top and in two portions, which fit together with a ground joint; an indentation encircles the inside of the cylinder at a convenient distance from the bottom, and carries a perforated porcelain or lead tray to carry the active material; it has a hole in the centre through which the stem of the acid reservoir passes in the usual manner.

The advantages claimed for this apparatus are: (1) accessibility of all parts for cleaning and recharging; (2) stability, as it is not so tall as the usual forms; (3) an even distribution of the active material over a relatively large area.

F. M. G. M.

Weighing. OTTO KUHN (*Chem. Zeit.*, 1910, 34, 1097—1098, 1168—1169).—Neglect to reduce the weighings of crucibles and other chemical apparatus to the weight in a vacuum may cause an error of several tenths of a milligram if the atmospheric conditions vary between two weighings. The correction should therefore be made in analytical work. Double weighing should be employed in order to eliminate errors due to unequal expansion of the arms of the balance.

C. H. D.

Inorganic Chemistry.

The Molecular Weight of Water in Different Solvents.

GIUSEPPE BRUNI and M. AMADORI (*Gazzetta*, 1910, 40 ii, 1-8).—Water is not sufficiently soluble in any hydrocarbon to permit of cryoscopic measurements, but a number of other solvents which might be expected to cause association have been examined. In each case the degree of association increases with the concentration, being very near to 1 in dilute solutions in bromoform, ethylene bromide, dimethyl-aniline, *p*-toluidine, methyl oxalate, methyl succinate, and veratrole. Alcohol, phenol, and acetic acid are associated in the same solvents, ethylene bromide having the greatest effect and methyl succinate the least. Alcohol and phenol, like water, form single molecules in dilute solution, but acetic acid is associated even in very dilute solution in ethylene bromide. C. H. D.

Direct Synthesis of Volatile Hydrogen Compounds.

ALEXANDER CH. YOUNASOS (*Ber.*, 1910, 43, 2272-2274).—Not only can phosphorus, arsenic, antimony, and sulphur be transformed into their hydrides by heating with sodium formate, but also other elements, especially those which are volatile, and various compounds. The less volatile a substance is, the more difficult it is to reduce it.

If a compound is made up of two volatile components, both are reduced, giving the two hydrides; this is the case with the sulphides of phosphorus, arsenic, and antimony, and the phosphides of arsenic and antimony. If only one component is volatile, that alone is hydrogenised; for example, the phosphides, sulphides, arsenides, antimonides, selenides, and tellurides of the metals. A large number of chloro-, bromo-, iodo-, and fluoro-derivatives, especially those of the heavy metals, give the corresponding halogen hydrides. Nitrides of the metals give ammonia. Silicides, borides, and carbides are not reducible.

Selenium and tellurium form the hydrides when heated with sodium formate to 400°; the yield is limited, owing to the reverse reaction (decomposition) which takes place.

Hydrogen silicide is formed to a slight extent when an equimolecular mixture of amorphous silicon and sodium formate is heated at 1300°. The reaction takes place more readily when the silicon is dissolved in aluminium (2 parts of silicon to 60 of aluminium) and the temperature kept at 750°. Hydrogen boride is formed when the silicon is replaced by amorphous boron (1 part of boron to 25 parts of aluminium); it also results when a mixture of boron with sodium formate is heated in the electric arc. T. S. P.

Some Analogies between Derivatives of Oxygen and Nitrogen. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 94-101. Compare this vol., ii, 844).—The author amplifies and

extends the views put forward in the former paper as to the analogy displayed in many of their reactions between hydrogen peroxide, hydroxylamine, hydrazine, etc.

R. V. S.

Decomposition of Ozone by Ultra-violet Light. EVA VON BAHR (*Ann. Physik*, 1910, [iv], 33, 598—606).—When ultra-violet light from a quartz-mercury lamp is allowed to fall on ozonised oxygen, the ozone is decomposed. The rate of decomposition increases rapidly as the pressure on the gas is reduced. For a given intensity of the incident ultra-violet radiation, the ozone disappears at a rate which agrees with the requirements of the equation for a unimolecular change, if the pressure is kept constant. The velocity constant is nearly independent of the pressure when this exceeds 200 mm. of mercury, but for lower pressures the constant increases rapidly as the pressure falls.

In consequence of the decomposing action of ultra-violet light, the measurement of the absorption of ultra-violet radiation cannot be applied to the estimation of ozone at low temperatures. H. M. D.

Ozone. V. The Development of Heat in the Decomposition of Ozone. ANTON KAILAN and STEPHAN JAHN (*Zeitsch. anorg. Chem.*, 1910, 63, 243—250. Compare Abstr., 1909, ii, 37).—The oxygen, containing 10% of ozone, is led through a decomposition tube containing soda-lime, enclosed in a vacuum vessel as calorimeter containing water. A manganin spiral is also provided for heating the apparatus electrically in order to calibrate it. With this apparatus, a rise of temperature of 0.2° in ten to fifteen minutes may be measured to 0.001° . The corrected value for the development of heat in the decomposition of ozone at constant volume is 31,500 cal. per gram-molecule.

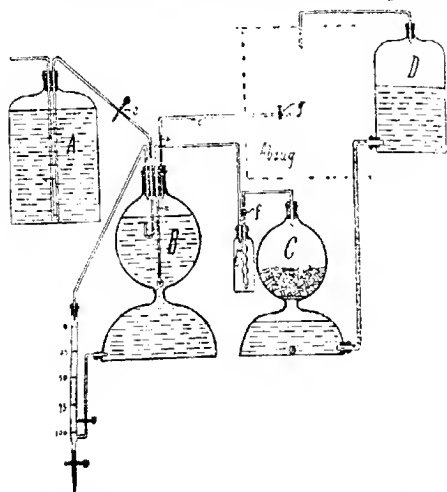
Experiments with other catalytic agents show that platinum-black gives high values, and rapidly loses its activity. With a heated platinum wire, which is easily calibrated, the concordant value 34,000 cal. per gram-molecule is obtained.

C. H. D.

New Hydrogen Sulphide Apparatus. STEFAN URBASCH (*Chem. Zeit.*, 1910, 34, 1040—1041).—The apparatus may be used in the laboratory room close to a fume chamber without causing any inconvenience whatever, and, owing to the high pressure, several solutions may be treated simultaneously with hydrogen sulphide.

A holds 5 litres, B altogether 6 litres, C altogether 4 litres, D also 4 litres. When used for the first time, B is filled with water, and a glass tube reaching to the bottom is introduced. C contains iron sulphide, D dilute hydrochloric acid (2:1). Hydrogen sulphide is now passed until the water in B is quite saturated, and the apparatus is then fitted up as shown in the figure. If the gas is wanted first, stopcock *f* and then stopcock *g* are opened, causing the acid to flow from D to C. The gas evolved enters by the tube *a* into B, passes through the water, and by means of the tube *b c* and stopcock *g* then passes through the solution to be tested. The gas current is easily regulated, and the spent acid is drawn off from the bottom of C. If saturated

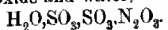
hydrogen sulphide water is required, it is allowed to drain from the burette, and the volume may thus be measured. Owing to the difference in level, fresh water flows from *A* into *B* until the former height has been again reached, and this water becomes again saturated with hydrogen sulphide. Not until 5 litres of hydrogen sulphide water have been used is there any need for replenishing the contents of *A*. During the passing of the gas, the siphon is closed, as otherwise a little of the solution might find its way into *A*. When no gas but only the solution is required,



no fresh water is introduced into *B*; the contents last a long time and cannot deteriorate. In order to empty the burette when the siphon is closed, it is necessary to open the pinchcock *f* for a moment. *B* is made of dark glass so as to prevent any decomposition by light.

L. DE K.

The Constitution of Weber's Acid. KONRAD W. JURISCH (*Chem. Zeit.*, 1910, 34, 1065—1066).—Objections are brought forward against the validity of the ordinary structural formulae for sulphuric acid and nitrosylsulphonic acid. The former is regarded as an additive compound of sulphur trioxide and water, and the latter as



Thermochemical reasons are given for supposing that the group SO_3 is present in both compounds, and that hydroxyl groups are absent.

C. H. D.

Action of Crushed Quartz on Nitrate Solutions. HARRISON E. PATTEN (*J. Physical Chem.*, 1910, 14, 612—619).—A filter bed was made with fine quartz flour of 740 sq. cm. area per gram, which was

washed with hydrochloric acid and distilled water. On percolating through it an 0.01*N*-solution of silver nitrate sterilised with chloroform, some silver remained on the quartz in an insoluble condition, and the filtrate contained upwards of 1% of nitrite calculated as silver nitrite. The silver remaining on the quartz, which was perhaps in the form of silver oxide or silver silicate, was soluble in ammonia, but the percolated silver nitrate was not tested for acidity.

The reduction of nitrate decreases as the adsorptive capacity of the quartz surface becomes satisfied. Sodium nitrate under sterile conditions is not reduced in contact with quartz to give any substance oxidisable with permanganate. The looser combination and the greater hydrolysis of the heavy metal nitrates may facilitate their reduction by quartz.

R. J. C.

The Hydration of Metaphosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1910, 63, 266—268. Compare this vol., ii, 607).—Although it is not found possible, on account of the volatility of metaphosphoric acid, to reach the temperature at which orthophosphoric acid would pass directly into the meta-acid, it is found that metaphosphoric acid in aqueous solution becomes directly hydrated to form the ortho-acid, without any intermediate formation of pyrophosphoric acid.

C. H. D.

Synthesis of Hydrogen Arsenide from its Elements. ALEXANDER CH. VOURNASOS (*Ber.*, 1910, 43, 2264—2272).—Dry nascent hydrogen, as prepared by heating sodium formate, readily combines with certain of the metalloids to form the hydrides of these elements (compare this vol., ii, 236). Hydrogen arsenide may be obtained by passing the vapours of arsenic heated to 460° over sodium formate contained in a tube heated to a temperature just below the decomposition point of the formate. The heat of the arsenic vapour completes the decomposition, and a mixture of hydrogen and hydrogen arsenide is obtained. The reaction is carried out much more conveniently by heating a mixture of three parts of powdered arsenic with eight parts of dry sodium formate rapidly to 400° in a round-bottomed flask. Yields of 12—17 volume % of hydrogen arsenide have been obtained.

Instead of using sodium formate alone, it is better to use an equimolecular mixture of sodium formate and sodium hydroxide or lime to prepare the nascent hydrogen, as this prevents the formation of sodium oxalate, and hence of carbon monoxide, when the temperature is raised too high. Moreover, arsenious oxide, sodium arsenite, or arsenic acid may be used in place of arsenic. When a mixture of equal weights of sodium formate and normal sodium ortho-arsenite is heated to temperatures not exceeding 400°, a gaseous mixture of hydrogen arsenide and hydrogen is obtained containing not more than 2—3% of the latter gas.

One great advantage of this reaction is that sulphur compounds and other inorganic and organic compounds of arsenic, for example, solid hydrogen arsenide, Schweinfurt green, arsenic trisulphide, arsenic-containing magenta, etc., all give arsenic trihydride when heated with

sodium formate, or with a mixture of sodium formate and sodium hydroxide. Marsb's test may thus be carried out without it being necessary to transform the arsenic compound into one of its oxygen derivatives. Organic compounds are best destroyed by oxidation with nitric and sulphuric acids, and the dry residue, which may still contain carbon, beated directly with the formate mixture. In some cases, it is an advantage to transform the arsenic acid produced by the oxidation into arsenic sulphide before further treatment. This is best done by means of pure hydrogen sulphide prepared by heating ten parts of the formate-hydroxide mixture with three parts of flowers of sulphur to 400° .

Urine which is to be tested for arsenic is made strongly alkaline and evaporated to dryness, the residue then being treated as above. Acids are first neutralised, and then evaporated, etc. Aniline dyes and textiles dyed with colours containing arsenic can be treated directly with the formate-hydroxide mixture, since organic matter does not affect the reaction, but it is better first to isolate the arsenic as chloride by distillation, and then transform it into the sulphide, or else to destroy the organic matter by fusion with sodium nitrate.

By the above methods it is possible to detect 0.001 mg. of arsenic.

A mixture of antimony oxide and sodium formate gives no trace of hydrogen antimonide when beated to 400° , metallic antimony alone being formed. When, however, sodium antimonite is used instead of antimony oxide, and the mixture rapidly heated to 800° , small quantities of the hydride of antimony are formed. This compound is also produced to a slight extent when metallic antimony is used and the mixture heated to a bright red heat. Antimony tri- and pentasulphides simply give rise to metallic antimony and hydrogen sulphide at 400° . Thus arsenic may be separated from antimony in their compounds by heating with the formate-hydroxide mixture to 400° , the antimony remaining behind in the metallic form. At 800° , however, some antimony also volatilises as the hydride. T. S. P.

Percarbonates. ERNST H. RIESENFELD (*Ber.*, 1910, 43, 2594—2595).—Polemical. A reply to Tanatar (compare this vol., ii, 33, 203, 290, 774). T. S. P.

Silicon Monosulphide. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 294—300).—When silicon (in the form of ferro-silicon) and sulphur are heated together in an electric arc furnace, a vigorous reaction takes place, and a grey mass results, from which, by sublimation in an electric furnace, silicon monosulphide may be obtained. The compound sublimes at 940 — 980° at 20 — 30 mm., and it occurs in two forms, namely, a black solid which may assume a vitreous character, and a yellow powder. On resublimation of either form, both are produced, the yellow one being deposited in the colder parts of the tube employed. Analysis of either product leads to the formula SiS , and the substance does not appear to be a mixture. The black modification has D_4^{25} 1.853. With alkalis, the compound reacts according to the equation $\text{SiS} + 2\text{KOH} = \text{SiO}_2 + \text{K}_2\text{S} + \text{H}_2$. The black sulphide dissolves in water with evolution of hydrogen sulphide and

formation of soluble silica, and of a finely-divided orange substance, which appears to be related to the oxygenated silicon hydrides of Wöhler (*Annalen*, 1863, 127, 257). It decomposes slowly in water, more rapidly in alkalis, with evolution of hydrogen and formation of silica. It dissolves in hydrofluoric acid, hydrogen being evolved, but it is insoluble in other acids. The yellow sulphide is also hydrolysed with evolution of hydrogen sulphide, but instead of soluble silica and the compound just described, a white, insoluble substance is formed, which yields hydrogen when treated with alkalis.

R. V. S.

The Equilibrium Diagram of the Silver-Cadmium Alloys. GIUSEPPE BRUNI and E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, 68, 198—206).—Silver and cadmium are melted together in an atmosphere of nitrogen. The diagram obtained is simpler than that of Rose (Abstr., 1905, ii, 86), although agreeing with it in the form of the liquidus. From 0 to 80 atomic % of cadmium, the alloys form a continuous series of solid solutions. The crystallisation intervals increase from 0 to 40 atomic % Cd, diminish to zero at 50%, increase to 60%, and again reach zero at 80% Cd. This indicates the existence of two compounds, AgCd and AgCd₂, both of which form solid solutions. This part of the curve resembles that of the magnesium-cadmium alloys (Grube, Abstr., 1906, ii, 355). The compound AgCd undergoes a transformation at 433°.

From 80 atomic % Cd to 97%, crystals of AgCd₂ separate, and from this point onwards solid solutions are formed. There is no eutectic point, the freezing point of cadmium being raised by the addition of silver, even in minute proportion.

G. H. D.

Peptisation of Silver Bromide. RAPHAEL E. LIESEGANG (*Zeitsch. Photochem.*, 1910, 9, 60—64).—A theoretical paper in which the author discusses the nature of the changes involved in the granulation and peptisation of the silver haloids.

H. M. D.

Silver Nitrate Formed by the Action of Nitric Acid on Silver Sulphide. HIPPOLYTE GRUENER (*J. Amer. Chem. Soc.*, 1910, 32, 1030—1032).—Boiling nitric acid of concentration above 5% dissolves silver sulphide rapidly, forming silver sulphate and nitrate. Acid stronger than 94%, however, forms only the sulphate. The maximum amount of nitrate (95%) is obtained by the use of 15—20% acid, greater dilution than this resulting in a smaller percentage. The production of the nitrate is diminished by boiling the acid or prolonging its time of action.

W. O. W.

Action of Potassium Hydroxide on Normal Calcium Phosphate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 662—664).—Normal calcium phosphate is not acted on when heated with a large excess of potassium hydroxide at 96—97° for fifty hours.

T. S. P.

The Binary Systems of Calcium Metasilicate with Calcium Chloride and Calcium Fluoride. B. KARANDÉEFF (*Zeitsch. anorg. Chem.*, 1910, 68, 188—197).—Mixtures of calcium carbonate, silica, and calcium fluoride are melted in a carbon tube and subjected to thermal analysis, the porcelain tube of the thermo-couple being protected with a layer of tar and graphite. Calcium metasilicate and calcium fluoride form a simple eutectiferous series, with a eutectic point at 48 molecular % CaF_2 and 1130° . The conversion of pseudowollastonite into wollastonite on cooling may be followed microscopically, but does not produce any thermal effect.

The eutectic point in mixtures of calcium metasilicate and calcium chloride lies close to the calcium chloride point, and 8° below it. Solid solutions may be formed up to 10 molecular % CaCl_2 . There is no evidence of the formation of additive compounds.

C. H. D.

Metallic Strontium. BEN L. GLASCOCK (*J. Amer. Chem. Soc.*, 1910, 32, 1222—1230).—A study has been made of the conditions necessary for the preparation of strontium by the electrolysis of its fused chloride. A quantity of the metal was prepared in the following manner. A hemispherical, cast-iron vessel of 25 cm. diameter was used as a container, and a carbon anode 8 cm. \times 8 cm. was employed. With pure strontium chloride as electrolyte, and a current of 125 amperes and 40 volts for seven hours, 76 grams of strontium were obtained, giving a current efficiency of 5.3%. The metal thus obtained had a purity of 97—98.5%, D 2.55, and specific heat 0.0742.

Strontium is a very light, soft metal, which has a silvery lustre when freshly cut, but rapidly becomes yellow and afterwards coated with a white layer of oxide. It reacts with water, methyl, and ethyl alcohols, ethyl acetoacetate and malonate, and aniline with evolution of hydrogen, and also reacts slowly with boiling ethyl iodide. The metal is without action on silicon tetrachloride. It dissolves readily in liquid ammonia, forming a deep blue solution from which a dark blue precipitate separates. It burns in an atmosphere of carbon dioxide and illuminating gas as energetically as in air, but not so violently as calcium does under similar conditions. When hydrogen and nitrogen are passed over the heated metal, the hydride and nitride are formed. An alloy of strontium and iron has been prepared and is described.

E. G.

The Ternary Alloys of Magnesium, Zinc, and Cadmium. I. GIUSEPPE BRUNI, G. SANDONNINI, and E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, 68, 73—90).—Magnesium and zinc form a single compound, MgZn_2 , and no solid solutions. On the other hand, zinc and cadmium form a simple eutectiferous series, whilst magnesium and cadmium form a compound, MgCd , which forms a continuous series of solid solutions with both components. It is found that the system MgZn_2 -Cd behaves like a binary system, and the present investigation includes the alloys of the ternary group MgZn_2 -Cd-Zn, leaving the remainder for a second part.

In the zinc-cadmium series, the eutectic point is at 262° and 73.5 atomic % Cd, and cadmium holds about 3 atomic % Zn in solid

solution. The eutectic point between Zn and $MgZn_2$ lies at 363° and 75 atomic % Mg. The eutectic point $Cd-MgZn_2$ lies at 280° and 80.05 atomic % Cd.

The ternary series examined is therefore of a simple type, having three binary eutectic lines and a ternary eutectic point, the last lying at 250° and 73 atomic % Cd, 25% Zn, and 2% Mg.

The total number of alloys examined in this section of the system is 103.

C. H. D.

Chemical Analyses of Minoan Metals from the Excavations of Crete. ANGELO MOSCO (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 225-228).—Of six samples of lead of Minoan origin only one contained tin (1.460%). It is suggested that the absence of tin objects in the Minoan remains is to be ascribed to the action of the "tin pest." A piece of gold was found to be alloyed with 20% of silver, this alloy being the so-called electron. A piece of silver was found to contain 20% of copper. The two pieces of electron and the piece of silver analysed belong to the third Middle Minoan Period (Evans' classification). A sphere of mineral examined was found to be an emery of the composition:

| Al_2O_3 . | Fe_2O_3 . | CaO. | MgO. | SiO_2 . | Total. |
|-------------|-------------|------|------|-----------|--------|
| 55.40 | 38.60 | 1.50 | 0.54 | 3.70 | 99.74 |

R. V. S.

Antique Glass Mirror. FRANZ W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1910, 31, 781-784).—Chemical investigation of an antique glass mirror found in a large Roman grave-yard in the Wiener Strasse in Leibach shows that it was made by pressing lead foil on to the glass, some kind of balsam being used as an adhesive. In the course of centuries the balsam has resinified and entered into combination with the lead, the lead thereby being converted for the most part into red lead. The lead forming the frame and hinder part of the mirror was changed on the surface into the basic carbonate.

T. S. P.

The Influence of Light on White Lead Blackened by Hydrogen Sulphide. ERNST TÄUFER (*Chem. Zeit.*, 1910, 34, 1126).—Contrary to the results of Sacher (this vol., ii, 712), the author finds that lead sulphide in white lead paints is bleached by the action of light, even in the absence of oxygen. The action is attributed to the peroxides of the drying oils in the paints. A blackened surface of white lead, coated in places with poppy-seed oil, is bleached by light only in the parts coated with oil. Freshly painted surfaces are even bleached in the absence of light, although more slowly.

C. H. D.

Crystallisation of Fused Lead Silicates. SIEGFRIED HILPERT and RICHARD NACKEN (*Ber.*, 1910, 43, 2565-2573. Compare Abstr., 1909, ii, 890).—The authors describe various apparatus by means of which they have taken the cooling curves of fused mixtures of lead oxide and silica, the fused mass being vigorously stirred during the cooling, and have measured the velocity of crystallisation and the crystallisation power (number of nuclei formed) of such fusions at

different temperatures. The results obtained are combined in a freezing-point diagram for mixtures varying in composition from lead monoxide to lead metasilicate. At first sight the curve seems to comprise two eutectics and one maximum, the latter corresponding with lead orthosilicate, m. p. 740° . The eutectics, however, correspond with the compositions $3\text{PbO}, 2\text{SiO}_2$ and $3\text{PbO}, \text{SiO}_2$, and further careful experiments (cooling curves, measurements of velocity of crystallisation, and microscopic examination of thin sections) with mixtures of these compositions show that the first supposed eutectic really consists of two eutectics close together, with a small maximum in between, corresponding with the compound $3\text{PbO}, 2\text{SiO}_2$, m. p. about 690° . The evidence for the second compound, $3\text{PbO}, \text{SiO}_2$, is not so satisfactory, but the examination of thin sections points to its existence.

T. S. P.

Ternary Alloys of Copper, Antimony, and Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 197—201, 243—247. Compare this vol., ii, 779, 852).—The first paper contains the experimental results obtained for the ternary systems Cu_3Sb — Sb — Bi , and the diagram of the system constructed with their aid.

In the second this diagram is discussed. Microscopic examination of the alloys has confirmed the results obtained by thermal method, and photomicrographs of some of the typical appearances observed are reproduced in this paper.

R. V. S.

Compounds of Nitric Oxide with Cupric Salts. WILHELM MANCHOT (*Annalen*, 1910, 375, 308—315. Compare Kohlshütter, *Abstr.*, 1904, ii, 734; Manchot, this vol., ii, 137). It has long been known that a solution of copper sulphate in concentrated sulphuric acid develops a violet or bluish-violet coloration with nitric oxide. The author shows that the coloration is due to the formation of an easily dissociable compound of 1 mol. each of copper sulphate and of nitric oxide. Its formation is influenced by the concentration of the water and of the copper salt present. No coloration or absorption of nitric oxide can be detected when sulphuric acid containing less than 70.8% of H_2SO_4 is used, whatever the concentration of the copper sulphate. At 0° and 752 mm., solutions containing 0.0053 to 0.0265 mol. of CuSO_4 per litre of 97.6% sulphuric acid absorb exactly 1 mol. of nitric oxide per 1 atom of copper; with greater concentrations of copper sulphate the amount of nitric oxide absorbed is less. A solution containing about 0.0175 mol. of CuSO_4 absorbs only 1 mol. of nitric oxide per 1 atom of copper when the pressure of the nitric oxide is increased from 322 mm. to 1303 mm.

Similar results are recorded for alcoholic solutions of hydrated cupric chloride. The dark violet compound is even more sensitive than the preceding to the decomposing action of water, for even in absolute alcohol solutions containing 0.005 to 0.1352 mol. of CuCl_2 per litre absorb only 17 to 18 litres of nitric oxide (at 0° and 750—753 mm.) per 1 atom of copper.

When dry hydrogen chloride is led into liquid nitric oxide cooled by liquid air, or when nitric oxide is passed into liquid hydrogen chloride, a dark red liquid is formed, which rapidly solidifies to a dark red, crystalline mass; the substance decomposes, however, even at the temperature of a mixture of solid carbon dioxide and acetone.

C. S.

Atomic Weight of Mercury. II. C. W. EASLEY (*J. Amer. Chem. Soc.*, 1910, 32, 1117—1126).—In an earlier paper (Abstr., 1909, ii, 1013), the atomic weight of mercury was determined by a study of the ratio $\text{HgCl}_2 : 2\text{AgCl}$. In order to confirm the value thus obtained, estimations were made of the mercury in mercuric chloride by precipitating mercuric oxide with sodium hydroxide and reducing it by means of hydrogen peroxide. Although the results of these experiments agreed closely with those obtained by the former method, the difficulty of collecting the mercury completely rendered the process untrustworthy.

Determinations have now been made of the ratio $\text{HgCl}_2 : \text{Hg}$ by the electrolysis of a solution of mercuric chloride. A special method was devised in which the metal was deposited in globular form by means of a mercury cathode, and, without being removed, was washed by decantation, freed from water by means of acetone, and afterwards weighed. The results of five preliminary experiments and of six final experiments each gave a mean value for the atomic weight of mercury, 200.63 ($\text{Cl} = 35.46$), whilst the value obtained in the earlier paper (*loc. cit.*) from the ratio $\text{HgCl}_2 : 2\text{AgCl}$ was 200.62.

E. G.

Ultra-microscopic Observations of the Hydrolysis of Mercuric Chloride. HERMANN W. FISCHER and E. BRIEGER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 196—197).—An aqueous solution of mercuric chloride has been found to contain a number of ultra-microscopic particles. These are attributed to the formation of a colloidal substance as a result of hydrolytic decomposition. The colloidal product ages with time, and becomes less soluble; this leads to further hydrolytic decomposition and to an increase in the number of ultra-microscopic particles. Rise of temperature has the same effect, and this observation supports the view that the presence of sub-microns is due to hydrolysis. The protective influence of sodium chloride on a solution of mercuric chloride is attributed to the diminution of the hydrolysis in consequence of the formation of the complex salt Na_2HgCl_4 .

H. M. D.

Lutetium and Neoytterbium or Cassiopeium and Aldebaranium. GEORGES URRAIN (*Zeitsch. anorg. Chem.*, 1910, 68, 236—242).—Claim for priority against Welsbach (Abstr., 1908 ii, 591; compare Abstr., 1908, ii, 283, 849).

C. H. D.

The Preparation of Manganio Fluorides and the Titration of Manganese by Volhard's Method in Presence of Fluorides. ERICH MÜLLER and PAUL KORPE (*Zeitsch. anorg. Chem.*, 1910, 68, 160—164).—Manganic fluoride has been prepared previously from

manganous oxide and hydrofluoric acid. A fluoride of tervalent manganese is readily obtained by the action of permanganates on a manganous salt in presence of hydrofluoric acid, the reaction being: $\text{MnO}_4^- + 4\text{Mn}^{++} + 8\text{H}^+ = 5\text{Mn}^{+++} + 4\text{H}_2\text{O}$. The difference between the reactions in presence of hydrofluoric and sulphuric acids is due to the conversion of Mn^{+++} into a complex fluoride ion in the former case.

By mixing, in the order given, a solution of 8.9 grams of manganous sulphate in 30 c.c. of water, 8 c.c. of 40% hydrofluoric acid, a solution of 1.58 grams of potassium permanganate in 25 c.c. of water, and one of 5.8 grams of potassium fluoride in 20 c.c., in a platinum basin, a salt is obtained which, after washing with hydrofluoric acid and alcohol and drying in a desiccator, has the composition $2\text{KF}, \text{MnF}_2, \text{H}_2\text{O}$.

Manganese dioxide, which is insoluble in hydrofluoric acid, dissolves if a manganous salt is also present. Manganic fluoride, free from potassium, may be obtained by electrolysis of a neutral solution of a manganous salt and dissolving the oxide precipitated at the anode in hydrofluoric acid.

The difficulty of observing the end-point in presence of the pink manganic salt makes it impossible to obtain accurate results on titrating manganese with permanganate in presence of hydrofluoric acid. The reaction appears, however, to be nearly complete in a warm solution. The presence of fluorides causes a large error in the titration of manganese by Volhard's method, but not in the titration of ferrous salts.

G. H. D.

Electrolytic Conversion of Manganates into Permanganates. KURT BRAND and J. E. RAMSBOTTOM (*J. pr. Chem.*, 1910, [ii], 82, 336—396).—The authors have been forestalled by Askenasy and Klonowsky (this vol., ii, 413) in the publication of their results. The manganate melt for the electrolytic production of potassium permanganate is made by heating manganese dioxide, potassium hydroxide, and a little water at a dark red heat, oxygen being supplied by the atmosphere and not by potassium nitrate or chlorate, since the addition of the latter results in the formation of potassium nitrite or chloride, the presence of either of which during the electrolysis is disadvantageous.

The apparatus consists of a slender glass vessel containing an earthenware vessel in which are the anode of nickel gauze and the anodic liquor, consisting of a solution containing 4% of potassium manganate and 14% of potassium hydroxide; the cathode is also made of nickel, and the surrounding solution is 2.2% potassium hydroxide. The results of the experiments show that the yield of potassium permanganate is appreciably increased by stirring thoroughly the anodic solution, and decreases with increase of the current density at the anode, the highest practicable value being 0.0125 ampere per sq. cm. with a nickel anode, and 0.005 with an iron anode.

The solubility of potassium permanganate in aqueous potassium hydroxide of varying strength has been determined, and it is shown

that the potassium permanganate remaining dissolved in the anodic liquor can be isolated, either by evaporating the solution carefully, protected from dust particles, etc., or by continually adding the solid manganate melt to the anodic solution during the electrolysis, whereby the concentration of the potassium hydroxide becomes ultimately so great that the potassium permanganate is almost entirely precipitated.

C. S.

The System Iron-Nickel. RUDOLF RUER and EMIL SCHÜZ (*Metallurgie*, 1920, 7, 415—420).—The freezing-point curve of the system iron-nickel, determined from quantities of 150 grams, is continuous, with a shallow minimum, and the liquidus and solidus curves practically coincide throughout. Determinations of the temperatures of magnetic transformation yield results in general agreement with those of Guillaume and Osmond, but the boundary between the reversible and irreversible alloys is now placed at 29% of nickel. The maximum of the reversible transformation curve at 618° and the minimum of the freezing-point curve at 1435° both lie near to 70% of nickel, pointing to the existence of a compound FeNi_2 .

The electrical conductivity of rods cast in narrow magnesia cylinders and annealed by heating to 900° and cooling slowly, shows a minimum at 35% Ni, and the compound FeNi_2 is not indicated on the curve.

C. H. D.

Goldschmidt's Ferroboron and Manganese-Boron, and the Residue Obtained on Heating Ferroboron in Hydrogen Sulphide. JOSEF HOFFMANN (*Chem. Zeit.*, 1910, 34, 1045—1046. Compare this vol., ii, 508).—Goldschmidt's borides behave towards reagents as heterogeneous substances, and this view is confirmed by microscopical examination, which shows distinct crystallites in a homogeneous ground mass. Detailed descriptions of some of the crystals are given.

The residue obtained when hydrogen sulphide acts on ferroboron contains borides which are resistant to acids, and also boron sulphide and a sulphur compound which is not ferrous sulphide, but probably a ferrous thioboride.

C. H. D.

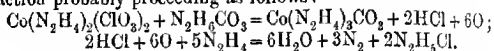
Complex Compounds of Cobalt with Chloric and Perchloric Acids. ROBERTO SALVADORI (*Gazzetta*, 1910, 40, ii, 9—18).—A number of cobaltiammine chlorates and perchlorates have been examined. They are all explosive, the chlorates by percussion or on ignition, the perchlorates by percussion or detonation. The perchlorates are very stable at the ordinary temperature, whilst the chlorates decompose slowly, the luteo-derivatives being more stable than the roseo- or purpureo-compounds.

For the analysis, the chlorates are reduced by means of ferrous sulphate in ammoniacal solution, and the perchlorates by fusion with sodium carbonate in a platinum crucible placed in an outer crucible also containing sodium carbonate. Ammonia is estimated by distillation with sodium hydroxide, and cobalt by electrolytic reduction in presence of ammonium oxalate. The metallic deposit contains carbon,

and it is necessary to dissolve it in sulphuric acid, to filter, and to re-deposit the cobalt electrolytically.

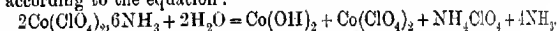
Luteo-cobaltiammine chlorate, $\text{Co}(\text{NH}_3)_6(\text{ClO}_3)_3 \cdot \text{H}_2\text{O}$, prepared by passing oxygen through a 5% solution of cobalt chloride in an excess of ammonia at 50° , adding chloric acid, and evaporating, forms yellow crystals, and explodes at 120° if rapidly heated. It may be obtained in an anhydrous form from luteo-cobaltiammine chloride and silver chlorate by cooling the filtrate in a freezing mixture. It then forms yellow needles, soluble in water to the extent of 7.87% at 18° , much more at higher temperatures.

Cobalthydrazine perchlorate, $\text{Co}(\text{N}_2\text{H}_4)_2(\text{ClO}_4)_2$, obtained by adding hydrazine hydrate to luteo-cobaltiammine chloride, forms yellow crystals, which are highly explosive. If carbon dioxide is passed into the solution containing hydrazine hydrate, cobalthydrazine carbonate and hydrazine hydrochloride are formed, and nitrogen is evolved, the reaction probably proceeding as follows:



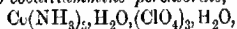
Roseo-cobaltiammine chlorate, obtained from the mother liquor of the luteo-salt, or from silver chlorate and roseo-cobaltiammine chloride, is a pink, very soluble powder, the solubility in water at 18° being 105.8%. The *purpureo*-salt, also obtained by double decomposition, forms large, garnet-red tetrahedra.

Cobalt perchlorate, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, prepared from cobalt carbonate and perchloric acid, and crystallised slowly, forms prisms 4 cm. long, loses water at 100° to form a violet, hygroscopic powder, and explodes by percussion. When rapidly heated, it deflagrates without exploding. When ammonia and ammonium perchlorate are added to its solution, a red powder having the composition $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$ is precipitated, ammonia directly replacing water. Boiling water decomposes it according to the equation:



Other metallic perchlorates behave in a similar manner.

Luteo-cobaltiammine perchlorate, $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, is soluble in water to the extent of 0.967% at 18° (compare Alvisi, Abstr., 1902, ii, 24). *Roseo-cobaltiammine perchlorate*,



and the *purpureo*-salt dissolve in water at 18° to the extent of 7.4% and 11% respectively. C. H. D.

Compounds of Chromium. VIII. Triamminechromium Salts. ALFRED WERNER (*Ber.*, 1910, 43, 2286—2295).—The starting point in the preparation of triamminechromium salts is triamminechromium tetroxide, for which a new method of preparation is given. To a strongly cooled solution of 30 grams of chromic acid in 300 c.c. of water are added 300 c.c. of pyridine. After remaining for half an hour in a freezing mixture, 750 c.c. of 3% hydrogen peroxide are added. The precipitated pyridine perchromate is collected, washed, and added to 90 c.c. of well-cooled 25% ammonia. The precipitated triamminechromium tetroxide is collected after ten minutes and washed with water, alcohol, and ether.

Trichlorotriamminechromium, $(\text{NH}_3)_3\text{CrCl}_3$, results when triamminechromium tetroxide is added to cold concentrated hydrochloric acid. A grey to bluish-grey precipitate is formed, and the filtrate from this deposits the trichlorotriamminechromium on keeping for two days. The crystals are dark blue with a greenish tinge. It is almost insoluble in water, in which properties it resembles trichlorotriamminecobalt. It dissolves in hot water, giving a blue solution, from which the dichloroaquatriamminechromium salts (Abstr., 1906, ii, 760) are precipitated by appropriate reagents. The grey to bluish-grey precipitate mentioned above is probably a mixture of dichloroaquatriamminechromium chloride and trichlorotriamminechromium.

Triaquatriamminechromium chloride, YCl_3 , where $\text{Y} = \left[\text{Cr} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{OH})_3 \end{smallmatrix} \right]$, is obtained as follows: A mixture of 1 gram of dichloroaquatriamminechromium chloride with 8 c.c. of water is covered with 5 c.c. of pyridine. The resulting solution is filtered, and the hydroxiodide precipitated by the addition of solid potassium iodide. The chloride is then obtained by triturating the hydroxiodide with concentrated hydrochloric acid. After purification by solution in water and precipitation with hydrogen chloride, it forms brownish-red, hygroscopic crystals. It was also prepared by dissolving triamminechromium tetroxide in dilute hydrochloric acid (1:4) and saturating the cooled solution with hydrogen chloride. The *chloride-nitrate*, YCl_2NO_3 , is precipitated when concentrated nitric acid is added to a cold concentrated solution of the chloride. When nitric acid is replaced by perchloric acid, pale red plates of the *perchlorate*, $\text{Y}(\text{ClO}_4)_3$, are obtained.

Dibromoaquatriamminechromium salts, YX , where $\text{Y} = \left[\text{Br}_2\text{Cr} \begin{smallmatrix} \text{OH}_2 \\ (\text{NH}_3)_2 \end{smallmatrix} \right]$. To prepare the *bromide*, YBr , triamminechromium tetroxide is dissolved in cooled hydrobromic acid (D 1.49), whereby bromine is evolved, and concentrated sulphuric acid added to the well-cooled solution. Intense green crystals are obtained, soluble in water to a green solution, which rapidly turns bluish-red. The *iodide*, YI , *thiocyanate*, YSCN , *nitrate*, YNO_3 , and *sulphate*, Y_2SO_4 , all form green crystals, and are prepared from a fresh solution of the bromide by precipitation with potassium iodide, potassium thiocyanate, nitric and sulphuric acids respectively. The green colour of these salts corresponds with that of the dichloro- and dibromo-diethylenediaminechromium salts. The dichloroaquatriamminechromium salts are, however, blue. This difference in colour is not due to a difference in constitution, since when the green dibromo-bromide is converted into triaquatriamminechromium nitrate, $\left[\text{Cr} \begin{smallmatrix} (\text{OH})_3 \\ (\text{NH}_3)_3 \end{smallmatrix} \right](\text{NO}_3)_3$, by means of silver nitrate, and the dichloroaquatriamminechromium nitrate prepared from this by means of hydrogen chloride, the usual blue salt is obtained. Both the green and the blue salts are therefore praseo-salts.

Bromodiaquatriamminechromium salts, YX_2 , where $\text{Y} = \left[\text{BrCr} \begin{smallmatrix} (\text{OH})_2 \\ (\text{NH}_3)_2 \end{smallmatrix} \right]$. Five grams of triamminechromium tetroxide are dissolved in 50 grams

of well-cooled hydrobromic acid (D 1.49). The solution is then boiled until bromine ceases to be evolved, cooled, and 80 c.c. of concentrated sulphuric acid added, whereby a brownish-red, crystalline deposit forms. If this is dissolved in water, the solution rapidly filtered, and the filtrate treated with concentrated hydrobromic acid, reddish-violet crystals of the *bromide*, YBr_3 , are obtained. With concentrated hydrochloric acid, the solution of the bromide gives reddish-violet crystals of the *chloride*, YCl_3 , from which salt the *sulphate*, YSO_4 , may be obtained as violet crystals. The transformation of the chloride into the sulphate proves that the bromine is in the complex.

Hitherto, it has not been possible to isolate the tribromotriammine-chromium, only the following three hydrates of the bromo-series being known, namely: $\left[\text{Br}_2\text{Cr}\left(\text{NH}_3\right)_3\right]\text{Br}$, $\left[\text{BrCr}\left(\text{OH}_2\right)_2\left(\text{NH}_3\right)_3\right]\text{Br}_2$, and $\left[\text{Cr}\left(\text{OH}_2\right)_3\left(\text{NH}_3\right)_3\right]\text{Br}_3$.

T. S. P.

The Behaviour of Iron towards Solutions of Stannous Salts. ALFRED THIEL and K. KELLER (*Zeitsch. anorg. Chem.*, 1910, 68, 220—235).—The fact that when iron is added to a solution of the chlorides of tin and antimony, only antimony is precipitated, is in contradiction to the positions of iron and tin in the electrochemical series. It is now shown that tin is actually precipitated, but only in very minute quantity, forming a very thin protecting layer of a tin-iron alloy on the surface of the iron.

Iron dissolves much less rapidly in an acid if a tin salt is present. Measurements of electrolytic potential show that in pure acid tin is always less noble than iron, the difference being greater in stronger acids. In acid containing a stannous salt the potential of iron varies, and finally assumes a value equal, or near, to that of tin, according to the conditions. The deposition of tin on iron is recognisable by analysis, if iron having a relatively large surface, such as turnings, is taken for the experiment.

If iron is introduced into a vessel containing a concentrated electrolyte, containing tin in the lower part, and a more dilute electrolyte free from tin in the upper part, the iron becomes covered with crystals of tin where it dips into the concentrated electrolyte, but remains free from tin if immersed completely in either the concentrated or the dilute solution.

O. H. D.

Atomic Weight of Tantalum. CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1910, 32, 1127—1133).—Owing to the uncertainty existing with regard to the value of the atomic weight of tantalum, determinations have been made of the ratio $2\text{TaCl}_5:\text{Ta}_2\text{O}_5$, the chloride being converted into the oxide by methods similar to those used in the determination of the atomic weight of columbium by Balke and Smith (*Abstr.*, 1908, ii, 1043).

Tantalum chloride was prepared by heating the oxide in a current of chlorine and vapour of sulphur chloride. The chloride was converted into the oxide in quartz bulbs. The bulbs containing the chloride

were placed in a vacuum desiccator with water, and the air was pumped out. The chloride gradually underwent hydrolysis; small quantities of water and concentrated nitric acid were then introduced into the bulb, and the mass was evaporated to dryness. The addition of water and nitric acid and the subsequent evaporation were twice repeated, and the dry mass was finally ignited until no further loss of weight occurred. The mean of eight experiments with three samples of the chloride gave a value for the atomic weight 181.52 ($\text{Cl} = 35.46$), whilst the value given in the international table of atomic weights is 181.0.

Tantalum chloride has D 3.68 at 27° . Specimens of the oxide prepared from the chloride had D varying from 7.91 to 8.62.

E. G.

Easy Method for Preparing Colloidal Gold. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 664—665).—A dilute solution of gold chloride containing a little starch is heated for a short time and then filtered. The filtrate is at first colourless, but gradually becomes deep violet in colour. The starch remaining on the filter paper is coloured violet, and after a few days presents a metallic reflecting surface. On exposing the violet filtrate to diffused light for some days, the gold is slowly deposited.

If the original solution of gold chloride and starch is gently heated for some minutes, the filtrate, which is opalescent, will reduce Fehling's solution.

T. S. P.

Mineralogical Chemistry.

A Method for Isolating Native Iron from Basalt without Destroying its Form. MAX SEEBACH (*Centr. Min.*, 1910, 641—643).

—Native iron occurs in the basalt of Bühl, near Weimar, in the form of a fine network. The basalt may be removed without destroying the form of the iron by heating with Plattner's flux (10 parts sodium carbonate, 13 parts potassium carbonate, 5 parts borax glass, and 5 parts dry starch) in a graphite crucible. In order to prevent the formation of a thin layer of oxide on the iron, charcoal may be mixed with the flux, and the whole covered with a layer of sodium chloride. A piece of basalt 1 c.c. in size is destroyed in one and a-half hours. The last traces of rock enclosed in the meshes of the iron are removed by fusion with boron trioxide. When it is only required to isolate the iron, without preserving its form, it is best to crush the basalt and fuse with boron trioxide.

C. H. D.

Diffusion of Crude Petroleum through Fuller's Earth. J. ELLIOTT GILPIN and OSCAR E. BRANSBY (*Amer. Chem. J.*, 1910, 44, 251—303).—Gilpin and Cram (*Abstr.*, 1909, i, 1) have shown that when petroleum is allowed to diffuse upwards through tubes packed

with fuller's earth, fractionation takes place, and the fractions rising to the top of the tubes are of lower sp. gr. than those at the bottom. The paraffin hydrocarbons collect in the upper parts of the tubes, and the unsaturated hydrocarbons in the lower parts.

A study has now been made of the behaviour of crude Illinois petroleum when treated in this way. Gilpin and Cram's results have been confirmed, and it has been found that the amount of the sulphur compounds, like that of the unsaturated hydrocarbons, increases gradually from the lightest oil at the top to the heavier oils at the bottom of the tube. When a solution of benzene in petroleum is allowed to diffuse through fuller's earth, the benzene, like the olefines and sulphur compounds, tends to accumulate in the lower part of the tube.

When fuller's earth, which has been used for such diffusion experiments and afterwards treated with water in order to remove as much oil as possible, is dried and extracted with ether, oils of high specific gravity and viscosity are obtained containing considerable quantities of unsaturated hydrocarbons and sulphur compounds. It is therefore evident that fuller's earth exercises a selective action on the petroleum.

A discussion is given of the causes of the differences between the various oils of the United States. Pennsylvania petroleum differs from those of Ohio, Texas, and California in containing a much larger proportion of paraffin hydrocarbons and a much smaller proportion of benzene, unsaturated hydrocarbons, and compounds of sulphur and of nitrogen. In view of the results of the present investigation, it is suggested that this difference may be explained by assuming that the Pennsylvania petroleum has diffused upwards through porous media, such as shales, limestones, and sandstones, and thus undergone fractionation, resulting in the removal of the unsaturated and aromatic hydrocarbons and the sulphur compounds. It is probable that the nitrogen compounds also behave like the unsaturated hydrocarbons and sulphur compounds, and this question is being studied. E. G.

Grahamite, a Solid Native Bitumen. CLIFFORD RICHARDSON (*J. Amer. Chem. Soc.*, 1910, 32, 1032—1049).—There is a regular gradation in properties and composition between paraffins, asphalt, manjaks, and grahamites, corresponding probably with different stages of metamorphism. The author discusses the relations between these minerals, and suggests that the term "grahamite" should be confined to that type of solid, native bitumen characterised by a schistose or hackly fracture, by its sparing solubility in naphtha, and by a high percentage of residual coke.

A list of occurrences of grahamite in America is given in tabular form, with the physical properties, percentage of bitumen, and ultimate composition of the bitumen. The bitumen from a typical grahamite from West Virginia gave C 86.56, H 8.68, and S 1.75%. The ash of grahamites contains vanadium, that of a specimen from the Inupson Valley containing 11—15% of V_2O_5 (compare Hewett, this vol., ii, 719). Trinidad bitumen should be classed as a grahamite rather than as a manjak. W. O. W.

Mosesite, a New Mercury Mineral from Terlingua, Texas. FREDERICK A. CANFIELD, WILLIAM F. HILLEBRAND, and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 202—208).—The mineral occurs as minute simple octahedra, or spinel-twins, on calcite, and is canary-yellow with an adamantine lustre. It is a mercury-ammonium compound with chlorine (about 5%) and sulphate (about 3.5% SO_4), being thus similar to kleinite (Abstr., 1907, ii, 788), but probably with mercurous, rather than mercuric, sulphate and chloride. In hydrochloric acid it is very slowly changed to calomel, whilst kleinite is completely, although very slowly, dissolved. Heated gradually in a bulb-tube, mosesite first changes colour to black, then to white, and at a higher temperature volatilises, giving sublimates of calomel and mercury. The crystals are optically birefringent, but they become isotropic at 186° ; on cooling they revert very slowly to the birefringent modification. Kleinite shows the same change from the optically birefringent to the isotropic state at a slightly higher temperature.

L. J. S.

The Synthetic Sapphires of Verneuil. ALFRED J. MOSES (*Amer. J. Sci.*, 1910, [iv], 30, 271—274).—The crystallised corundum of a fine sapphire-blue colour prepared artificially by A. Verneuil (this vol., ii, 212) gave, on analyses by M. A. Lamme, Al_2O_3 , 99.83—99.85%; TiO_2 , 0.11—0.13%; Fe_2O_3 , trace; SiO_2 , nil; D 3.977—4.01. Refractive indices (sodium-light), $\omega = 1.7680$, $\epsilon = 1.7594$. The pleochroism is distinct (ω , indigo-blue, ϵ , pale blue). The optical interference-figure varies from uniaxial to slightly biaxial in character, and the optic axis is inclined at about 40° to the axis of the conical mass.

L. J. S.

Lanthanite. GUSTAF LINDSTRÖM (*Jahrb. Min.*, 1910, ii, Ref. 15; from *Geol. För. Förh. Stockholm*, 1910, 32, 206—214).—Lanthanite of D 2.69—2.74, collected from cerite specimens from Bastnäs, Sweden, gave on analysis:

| $(\text{La}, \text{Di})_2\text{O}_3$ | Ce_2O_3 | Y_2O_3 | CO_2 | H_2O | Insoluble. | Total. |
|--------------------------------------|-------------------------|------------------------|---------------|----------------------|------------|--------|
| 28.34 | 25.52 | 0.79 | 21.95 | 23.40 | 0.13 | 100.13 |

This, like the analyses of American lanthanite, agrees with the formula $\text{R}_2\text{O}_{11} \cdot 3\text{CO}_2 \cdot 8\text{H}_2\text{O}$.

Hisinger's analysis of "hydrofluocerite" from Bastnäs has come to be wrongly quoted in the text-books under lanthanite, owing to the incorrect translation of the Swedish "flusspatssyra" as "carbonic acid" in an early abstract in *Edin. J. Sci.*, 1826.

L. J. S.

New Occurrence of Hydrogiobertite. ROGER C. WELLS (*Amer. J. Sci.*, 1910, [iv], 30, 189—190).—The material occurs in considerable amount as a white encrustation on shale in Chiles Valley, Napa Co., California, and has been deposited from the water of springs; the serpentine-rocks occurring in the neighbourhood probably supplied the magnesium. The structure is spherulitic, and the spherules often contain a nucleus of shale; D 2.152. Analyses of material containing

admixed shale gave the following results, agreeing with the hydrogiobertite formula: $2\text{MgO} \cdot \text{CO}_2 \cdot 3\text{H}_2\text{O}$.

| Insoluble. | (Al, Fe) ₂ O ₃ | CaO. | MgO. | CO ₂ | H ₂ O. | Total. |
|------------|--------------------------------------|------|-------|-----------------|-------------------|--------|
| 25.33 | 1.90 | 2.60 | 31.81 | 18.06 | 20.06 | 99.76 |
| 14.93 | 1.06 | 1.84 | 36.40 | 23.71 | 20.81 | 98.75 |

L. J. S.

Analyses of Minerals from Croatia. FR. TUČAN (*Jahrb. Min.*, 1910, ii, Ref. 39—41; from *Glasnik [Berichte] kroat. naturv. Ges., Agram*, 1907, 19).—I. Dolomite from the Fruška mountains; pale green, coarsely granular, from serpentine-rocks. II. Magnesite from the Bušnica stream near Trgove; milk-white, compact with conchoidal fracture, from serpentine-rocks. III. Magnesite from the Bečinski potok stream in the Fruška mountains; similar to the last. IV—VI. Strontianocalcite from Radoboj; fibrous aggregates associated with strontianite. VII. Hydrozincite from Ivanec in the Ivančica mountains; milk-white, reniform aggregates associated with smithsonite. VIII—X. Muscovite from the pegmatites at various localities in the Krndija mountains.

| | Al ₂ O ₃ | FeO. | MgO. | CaO. | SrO. | MgO. | CO ₂ | Insol. | Total. |
|-------|--------------------------------|-------|-------|-------|-------|-------|-----------------|--------|--------|
| I.* | 0.21 | 1.53 | 1.30 | 30.78 | trace | 19.47 | 46.80 | 0.10 | 102.19 |
| II. | 0.62 | 1.80 | trace | 0.37 | — | 41.93 | 47.29 | 8.61 | 100.67 |
| III.† | 0.57 | 4.39 | trace | 0.23 | — | 30.94 | 36.84 | 27.01 | 99.98 |
| IV. | — | trace | trace | 54.11 | 2.26 | — | 43.51 | 0.10 | 99.98 |
| V. | — | trace | trace | 40.59 | 19.32 | — | 40.05 | — | 99.94 |
| VI. | — | trace | trace | 53.07 | 3.66 | — | 43.26 | — | 99.99 |
| VII.‡ | — | 1.25 | — | 0.20 | — | — | 14.30 | — | 100.27 |

* NiO, trace. † Na₂O, K₂O, Li₂O, trace. ‡ ZnO, 73.75; H₂O, 10.71.

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | Li ₂ O. | H ₂ O. | Total. |
|-------|------------------|--------------------------------|--------------------------------|------|-------|------|-------|-------------------|--------------------|--------------------|-------------------|--------|
| VIII. | 47.72 | 28.70 | 7.24 | 0.58 | trace | 0.54 | — | 7.31 | 1.52 | trace | 6.54 | 100.35 |
| IX. | 46.93 | 34.32 | 3.18 | — | trace | 0.63 | 0.21 | 5.33 | 2.42 | trace | 3.83 | 99.91 |
| X. | 46.66 | 37.40 | 2.82 | 0.18 | trace | 0.53 | trace | 6.09 | 2.41 | trace | 1.93 | 100.47 |

L. J. S.

Chalybite from Croatia. FR. TUČAN (*Jahrb. Min.*, 1910, ii, Ref. 12; from *Nastavni vjesnik, Monatsber. kroat. Mittelschulver., Agram*, 1908, 17).—Fourteen analyses are given of chalybite from various localities in Croatia.

L. J. S.

New Occurrence of Plumbojarosite. WILLIAM F. HILLEBRAND and FRED. E. WRIGHT (*Amer. J. Sci.*, 1910, [iv], 30, 191—192. Compare Abstr., 1902, ii, 667).—The mineral was found at American Fork, Utah, as friable lumps consisting of minute, brownish-red, glistening crystals with pyromorphite and calcite. The crystals are rhombohedral, with the basal pinacoid largely developed, and a rhombohedron ($\sigma = 53^\circ 40'$ about); they are optically uniaxial and negative, and strongly dichroic. Analysis gave:

| Fe ₂ O ₃ . | PbO. | K ₂ O. | Na ₂ O. | SO ₂ . | H ₂ O. | CuO. | CaO. | Insol. | Total. |
|----------------------------------|-------|-------------------|--------------------|-------------------|-------------------|------|------|--------|--------|
| 42.87* | 18.46 | 0.15 | 0.52 | 27.67 | 10.14 | 0.10 | 0.06 | 0.40 | 100.37 |

* Including very little P₂O₅ and probably some Al₂O₃.

L. J. S.

Oxalite from Cape d'Arco (Island of Elba). ERNESTO MANASSE (*Atti. R. Accad. Lincei*, 1910, [v], 19, ii, 138—145).—The mineral was found in a vein of oxide and hydroxide of iron and manganese, which also contains pyrites and galena. It forms small, transparent prisms or tablets of an amber-yellow colour, hardness about 2, D 2.28. Analysis leads to the formula $\text{FeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$

| FeO. | MgO. | C ₂ O ₄ . | H ₂ O (by difference). |
|-------|-------|---------------------------------|-----------------------------------|
| 40.72 | trace | 40.18 | 19.10 |

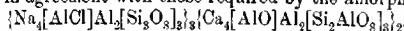
An oxalate of similar composition, but only microcrystalline, was prepared from ferrous ammonium sulphate or ferrous chloride, with oxalic acid. The crystallographic examination of the mineral gave $[a:b:c = 0.77297:1:1.10392]$. The crystals are birefractive to an unusual degree.

R. V. S.

Mizzonite from Cape d'Arco (Island of Elba). ERNESTO MANASSE (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 211—215).—The mineral was found in association with quartz in small veins of manganese oxide and hydroxide in a mine which yields iron and manganese. In close proximity occur crystalline schists and calcite of presilurian origin. It has hardness 5—6, and D 2.60. The crystals are prismatic, have a nacreous lustre, and are birefractive. Analysis gave:

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | Na ₂ O. | K ₂ O. | Cl. | Loss at red heat | Total. |
|--------------------|----------------------------------|----------------------------------|-------|-------|--------------------|-------------------|------|------------------|--------|
| 54.40 | 24.44 | trace | 10.19 | trace | 7.59 | 1.69 | 1.53 | 1.43 | 101.27 |

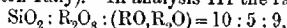
which is in agreement with those required by the amorphous mixture,



The values observed for the indices of refraction and the birefracton are also in accord with this structure.

R. V. S.

Minerals from Ruwenzori. LUIGI COLOMBA (*Jahrb. Min.*, 1910, ii, Ref. 41—42; from "*Il Ruwenzori*" by the *Duca degli Abruzzi*, Milano, 1909, 2, 281—286).—The minerals collected from the amphibolite, granite, and pegmatite are described, and analysis given of the following: I—IV, Epidote, as small, striated needles (I, greyish-green; II, pale green; III, brownish-green; IV, colourless, from Lake of Garda in northern Italy). In analysis III the ratio of



whilst in the others it is 2 : 1 : 2. V, Albite, as small crystal druses in crevices; VI, Microcline, massive; VII, Garnet (pyrope), as bright red, distorted crystals associated with microcline; VIII, Ilmenite, indistinct crystals, associated with albite:

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O. | Total. |
|------|--------------------|----------------------------------|----------------------------------|-------|-------|-------|-------------------|--------------------|-------------------|--------|
| I. | 38.21 | 30.84 | — | 7.25 | 20.43 | 0.38 | — | — | 2.71 | 99.82 |
| II. | 37.63 | 31.41 | — | 4.38 | 23.70 | — | — | — | 2.19 | 99.31 |
| III. | 38.31 | 23.47 | 12.29 | — | 23.52 | — | — | — | 2.42 | 100.01 |
| IV. | 37.95 | 30.38 | — | 7.83 | 20.34 | 0.93 | — | — | 2.64 | 100.07 |
| V. | 67.43 | 20.15 | — | — | 1.43 | — | — | 10.27* | — | 99.28 |
| VI. | 64.30 | 19.69 | — | — | — | — | 15.33 | 0.71 | 0.40 | 100.43 |
| VII† | 41.43 | 24.71 | 1.37 | 10.31 | 5.33 | 16.51 | — | — | — | 99.66 |

* With a little K₂O.

† MnO, trace.

| | TiO ₂ . | FeO. | Fe ₂ O ₃ . | MgO. | Total. |
|-------|--------------------|-------|----------------------------------|------|--------|
| VIII. | 52.73 | 45.83 | nil. | 1.25 | 99.81 |

L. J. S.

A Garnet containing Iron and Chromium from Praborna (St. Marcel). LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 146—150).—The mineral occurs in association with hematite, quartz, albite, and titanite, whilst native gold and kammererite are also to be found in the same situation. Analysis yielded the following figures:

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | Cr ₂ O ₃ . | CaO. | MgO. | MnO. | FeO. | Total. |
|--------------------|----------------------------------|----------------------------------|----------------------------------|-------|-------|------|------|--------|
| 35.57 | 0.62 | 22.22 | 7.81 | 27.13 | trace | 3.94 | 2.51 | 99.80 |

which correspond, when the small amount of aluminium is neglected, with the typical garnet composition $R_3(R_2)''^{VI}Si_3O_{12}$. From a comparison of the analytical data with those found for various specimens of uvarowite, the author considers it probable that this mineral also belongs to that group. It has D 3.81, and is very strongly birefractive.

R. V. S.

Gageite, a New Mineral from Franklin, New Jersey. ALEXANDER H. PHILLIPS (*Amer. J. Sci.*, 1910, [iv], 30, 283—284).—This is found in very small amount as delicate acicular and hair-like, colourless crystals arranged in radiating bundles, and is associated with zincite, willemite, calcite, and leucopheniceite. When heated, the clear crystals lose water and assume a deep bronze colour. Analysis by R. B. Gage gave:

| SiO ₂ . | MnO. | ZnO. | MgO. | H ₂ O. | Total. |
|--------------------|-------|------|-------|-------------------|---------|
| 24.71. | 50.19 | 8.76 | 11.91 | [4.43] | 100.00. |

Formula: $8RO \cdot 3SiO_2 \cdot 2H_2O$. The mineral appears to be closely related to leucopheniceite (Penfield and Warren, Abstr., 1900, ii, 89), and it is, perhaps, one of the undescribed species mentioned by Penfield and Warren.

L. J. S.

The Chemical Composition of the Stassfurt Salt Clays. E. MARCUS and WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1910, 68, 91—101).—The portion soluble in water is estimated by boiling with water and washing until no more chlorine passes through. The main analysis is made by Hillebrand's method. Water is estimated by heating with dried sodium carbonate or lead oxide in a current of air. The methods employed are described in detail. In the following analyses, arranged in order of depth, I is a hard salt clay, II a shaly salt clay, III a soft loamy clay, and IV a hard clay immediately in contact with the anhydrite.

Soluble in Water:

| | NaCl. | KCl. | MgCl ₂ . | K ₂ SO ₄ . | CaSO ₄ . | MgSO ₄ . |
|------|-------|------|---------------------|----------------------------------|---------------------|---------------------|
| I. | 0.36 | — | — | 16.94 | 36.11 | 12.08 |
| II. | 0.61 | 0.31 | 0.73 | — | 35.14 | 0.94 |
| III. | 1.09 | 0.40 | 5.41 | 0.33 | 1.19 | — |
| IV. | 0.23 | 0.16 | 1.44 | — | 0.92 | 0.71 |

Insoluble:

| | CaSO ₄ . | CaO. | MgCO ₃ . | MgO. | K ₂ O. | Na ₂ O. | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | Mn ₂ O ₃ . | ZnO. | SiO ₂ . |
|------|---------------------|------|---------------------|-------|-------------------|--------------------|----------------------------------|----------------------------------|------|----------------------------------|-------|--------------------|
| I. | 22.72 | 0.53 | — | 1.56 | 0.11 | 0.26 | 0.78 | 0.40 | 0.05 | — | trace | 2.98 |
| II. | 27.06 | 0.88 | — | 3.88 | 0.61 | 0.005 | 4.51 | 0.50 | 0.49 | — | 0.14 | 19.46 |
| III. | 0.87 | — | — | 10.41 | 2.53 | 0.33 | 17.04 | 2.00 | 1.56 | 0.27 | 0.11 | 37.80 |
| IV. | 0.70 | — | 75.43 | 0.54 | 0.29 | 0.09 | 2.16 | 0.37 | 1.51 | — | 0.10 | 11.17 |

| | TiO ₂ | P ₂ O ₅ | H ₂ O | C | CO ₂ | S | Vd ₂ O ₂ | Total (corrected). | Bitu- men. |
|------|------------------|-------------------------------|------------------|------|-----------------|-------|--------------------------------|-----------------------|---------------|
| I. | 0.05 | trace | 4.51 | 0.07 | 0.69 | trace | — | 100.22 | 0.11 |
| II. | 0.24 | 0.01 | 3.99 | 0.15 | 0.53 | trace | <0.02 | 100.21 | 0.15 |
| III. | 0.64 | 0.13 | 16.39 | 0.16 | 0.75 | 0.03 | 0.02 | 99.52 | 0.12 |
| IV. | 0.13 | 0.08 | 3.94 | 0.22 | — | 0.03 | <0.01 | 100.25 | 0.11 |

All contain traces of lithium and chromium, and all but (I) also contain small quantities of boric acid and bromine. The minute quantities of ammonia, nitrates, and copper have been recorded previously (Abstr., 1909, ii, 571, 1011). C. H. D.

The Amount of Thorium in Sedimentary Rocks. II. Arenaceous and Argillaceous Rocks. JOHN JOLY (*Phil. Mag.*, 1910, [vi], 20, 353—357).—Whereas the calcareous rocks show a small, almost negligible, quantity of thorium (compare this vol., ii, 723), the detrital sediments in almost every case contain easily measured amounts, the argillaceous group having almost double the amount in the arenaceous group. For the former 1.3, and for the latter 0.6 ($\times 10^{-5}$ gram per gram), may be taken as average values. Twelve specimens of arenaceous and conglomeritic rocks, mainly sandstones, were examined, and eighteen specimens of argillites, mainly slates. A specimen designated as "Grauwacke, Wipperfurth, Rhénus-Prussia, Middle Devonian" gave the highest result (2.4). The higher thorium content of the slates and shales is attributed to the sorting out by gravity of the large particles of quartz or felspar which are poor in radioactive constituents. F. S.

Physiological Chemistry.

Influence of a Rise of Body Temperature on the Blood Gases. WILHELM CASPARI and ADOLF LOEWY (*Biochem. Zeitsch.*, 1910, 27, 405—417).—At great altitudes (Monte Rosa) a rise of body temperature is very frequent, and symptoms of acidosis occur. The fall in the oxygen tension is compensated for by increased respiration, so that the oxygen in the tissues is but little affected; the elevation of body temperature and the acidosis are favourable factors for the dissociation of oxyhæmoglobin in the tissues. The body is thus able to compensate for the alterations in pressure. The heart is not affected. W. D. H.

The Gases of Cat's Blood. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1910, 41, 60—63).—Data of the gases in cat's blood are scanty; the authors used their new form of gas pump. The following are the mean figures of numerous analyses. In the third line the analyses were made with a Töpler-Barcroft pump; here the nitrogen values were between 1.5 and 4%; these have been adjusted to 1.00 to make the figures comparable to those in the first

line. The cats used were killed either by a blow on the head or were anaesthetised with urethane:

| | Total gas. | CO ₂ . | Oxygen. | Nitrogen. |
|----------------------|------------|-------------------|---------|-----------|
| Arterial blood | 39.68 | 25.07 | 13.60 | 1.00 |
| Venous blood | 51.53 | 40.83 | 9.93 | 0.77 |
| Arterial blood..... | 33.29 | 17.69 | 14.61 | 1.00 |

W. D. H.

Cryoscopy of Blood. W. R. G. ATKINS (*Bio.-Chem. J.*, 1910, 5, 215--216).—A few observations on the value of Δ for the blood of various animals; some amount of variation is noted, and in some cases this may have been pathological.

W. D. H.

The Inorganic Constituents of the Blood in Vertebrates and Invertebrates and Its Origin. ARCHIBALD B. MACALLUM (*Proc. Roy. Soc.*, 1910, B, 82, 602--624. Compare Abstr., 1904, ii, 495).—Analyses of the ash of the blood in various animals are given and compared with the saline contents of the ocean at various geological periods. The arguments advanced are speculative, but the facts so far as at present collected support the author's previous conclusion that the saline composition of the sea determines that of the blood of marine organisms, and that the inorganic composition of vertebrate blood-plasma is an heirloom of life in the primeval ocean. The date of the origin of the vertebrate kidney is placed between the second eighth and the second sixth of the whole geological period.

W. D. H.

Hæmolysis. Is there a Cocaine Hæmolysis? GEORG FISCHER (*Pflüger's Archiv*, 1910, 134, 45--58).—Cocaine solutions have no specific hæmolytic power, but such hæmolysis as occurs is due to dissociation and liberation of hydrogen ions, or to decomposition of the cocaine molecule and liberation of hydrogen ions and alcohol.

W. D. H.

Origin and Destiny of Cholesterol in the Animal Organism. VII. The Quantity of Cholesterol and Cholesterol Esters in the Blood of Rabbits Fed on Diets containing Varying Amounts of Cholesterol. MARY T. FRASER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1910, B, 82, 559--568).—When cholesterol is given with the food, some is absorbed, and the free cholesterol and the cholesterol esters in the blood are increased. If phytosterol is given, this substance is partly absorbed, and the free cholesterol of the blood rises. Phytosterol does not appear in the blood as such.

The digitonin method for estimating cholesterol is very accurate.

W. D. H.

Action of Acids and Alkalis on the Artificial Anti-serum of the Ox, which is Hæmolytic to Rabbits. GIOVANNI MORUZZI (*Biochem. Zeitsch.*, 1910, 27, 498--515).—Hydrochloric acid completely inhibits the hæmolysis when present to the extent of 0.015*N*; it does

not destroy the hæmolytic power, for this again becomes evident on neutralisation. There is no destruction either of the amoceptor or the complement. Dilution with normal saline solution does not revive the process. Similar experiments with sodium hydroxide show many analogies to the action of hydrochloric acid. There is no increase in viscosity in either case.

W. D. H.

The Relationship between the Anti-trypsin of the Blood and that of the Urine. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, 27, 397—404).—In artificial nephritis in rabbits there is a great rise in the anti-trypsin of the urine and of the blood. In nephritis produced by uranium salts, the rise is first seen in the urine; in that produced by chromic acid, first in the blood; in spontaneous albuminuria and in that produced by mercuric chloride, the rise in both fluids is simultaneous.

W. D. H.

Inhibition of Precipitation by Precipitoids. WILHELM SPÄT (*Biochem. Zeitsch.*, 1910, 23, 7—15).—The experiments described show that the inhibition of precipitation produced by inactivated immune serum or normal serum is not brought about by a union between the inactive serum (precipitoid) and extracts of bacteria employed.

W. D. H.

Estimation of Adrenaline in Normal Blood and after its Injection by means of Physiological Methods. PAUL TRENDELENBURG (*Arch. exp. Path. Pharm.*, 1910, 63, 161—176).—The physiological test adopted was in principle that of Laewen (*ibid.*, 1904, 51, 415), namely, the measurement of the vaso-constrictor effect on the frog's hind limbs by the rate of outflow when perfused with the substance dissolved in Ringer's solution. The quantity of adrenaline in the blood stream of cats after an injection runs parallel to its pressor effect. As the blood pressure falls, the amount of adrenaline in the circulation sinks. Adrenaline thus resembles muscarine in its rapid disappearance.

W. D. H.

Specific Adaptation of Digestive Juices. I. Specificity of Gastric and Pancreatic Juice. E. S. LONDON and W. N. LUKIN. II. Specificity of Duodenal Mixed Juices. E. S. LONDON and R. S. KRYM. III. E. S. LONDON and N. DOBROWOLSKAJA (*Zeitsch. physiol. Chem.*, 1910, 68, 366—377).—I. From experiments on fistulous dogs, varying kinds of food placed in the intestine lead to specific variations in the quantity of bile and pancreatic juice secreted, but not to variations in the amounts of the pancreatic enzymes. When fat is introduced, there is no increase (five cases out of seven) in the lipase secreted in the "small stomach."

II. The same is true for the mixture of juices in the duodenum when the food is introduced into the lower jejunum and ileum.

III. There is similarly no adaptation of the enzymes of the intestinal juice. Oleic acid and amino-acids are specially powerful stimulants in regard to the amount of juice secreted.

W. D. H.

The Laws of Digestion and Absorption. VI. The Distance Law of Solution by Duodenal Juice. E. S. LONDON and C. SCHWARZ. VII. The Neutralisation Laws of Digestive Juices. E. S. LONDON and O. J. GOLMBERG. VIII. The Action of Various External Factors on the Secretion of Duodenal Juices. IX. Digestion of Carbohydrates. E. S. LONDON and A. P. KORCHOW (*Zeitsch. physiol. Chem.*, 1910, 68, 346—351, 352—357, 358—362, 363—365. Compare this vol., ii, 422).—VI. By experiments on dogs with fistulae, it was found that the effect of an acid peptone solution in calling forth the secretion of the pancreas and liver is not limited to the duodenum, but extends as far as the upper ileum, a distance of about 2 metres; this action in stimulating secretion diminishes analwards with the square root of the distance from the point of stimulation.

VII. The quantity of pancreatic juice is directly proportional to the square root of the concentration of the gastric juice, and its alkalinity inversely proportional. The total amount of alkali in the duodenal juices is inversely proportional to the square root of the gastric juice concentration.

VIII. Further laws are laid down in regard to the duodenal juices (bile, pancreatic juice, intestinal juice), in all of which the square root figures largely.

IX. Three hours after a meal of flesh and starch in a dog, the stomach contents contain the same amount of starch, although the amount given varies from 40 to 100 grams. W. D. H.

The Chemistry of Digestion and Absorption in the Animal Body. XL. The Study of Gastric Digestion on a Mixed Protein Diet. E. S. LONDON and C. SCHWARZ (*Zeitsch. physiol. Chem.*, 1910, 68, 378—380. Compare this vol., ii, 422).—Gastric digestion is specially furthered by those proteins (such as meat compared with egg-white) which stay longest in the stomach. W. D. H.

Digestion of Fat in the Stomach and Small Intestine, and the Effect of Lecithin on it. USUKI (*Arch. exp. Path. Pharm.*, 1910, 63, 270—293).—If lecithin or egg-yolk is mixed with milk, the rate of fat digestion is increased, and the contents leave the stomach sooner. The addition of lecithin lessens the amount of soaps in the intestine, and increases it (after egg-yolk) in the faeces; this is explained by absorption processes in the large intestine. The splitting of lecithin in the stomach occurs more quickly than that of neutral fats. Lecithin favours the saponification and digestion of neutral fats. In spite of its small percentage of lecithin, fat digestion is more favoured by egg-yolk than by lecithin itself; this is probably due to the fineness of the emulsion as well as the chemical nature of the fat in yolk. No lecithin was found in the intestine; it must therefore be split up either in the stomach or soon after its entrance into the duodenum. The observations were made on dogs and children. W. D. H.

Phosphorus Metabolism in the Animal Organism. FELIX ROGOZIŃSKI (*Bull. Acad. Sci. Cracow*, 1910, B, 260—312).—Sodium

phosphate, phytin, and lecithin, added to the diet of a grown dog, produce no marked change in nitrogenous metabolism. Sodium phosphate is excreted quantitatively in the urine. Lecithin when given is not found in the faeces; its phosphoric acid appears quantitatively as inorganic phosphate in the urine; the phosphorus of phytin appears to the extent of 30% as phosphoric acid in the urine; the remainder is found as phytin in the faeces. In opposition to the work of others, phytin in man causes no change in the excretion of nitrogen or phosphorus; a small part of the phosphorus is retained; the remainder appears as inorganic phosphate in the faeces. In contrast with the dog, human faeces contain abundant lecithin compounds. No inositol is found in human urine after feeding on phytin. The bacteria of human faeces are able *in vitro* to decompose phytin and produce inorganic phosphates from it. W. D. H.

Physiological Protoplasmic Metabolism and Purine Formation. F. MAREŠ (*Pflüger's Archiv*, 1910, 134, 59—102).—The various theories of the origin of purine substances, especially uric acid (for instance, the muscular theory, the leucocyte theory, etc.), are discussed at length. Purely chemical views are discountenanced, for the source of purine is to be sought in the physiological activity of the living cell. The constancy of uric acid excretion in individuals is true only for fasting periods, and considerable stress is laid on the importance of the work of the digestive organs as a means of increasing uric acid formation. The nucleus of the cell is the main part concerned, and the same is true for other active cell masses, for instance, malignant growths. The importance of the digestive glands is shown by the fact that pilocarpin raises the uric acid output. W. D. H.

The Metabolism of Some Purine Compounds in the Rabbit, Dog, Pig, and Man. LAFAYETTE B. MENDEL and JOHN F. LYMAN (*J. Biol. Chem.*, 1910, 8, 115—144).—The examination of tissue extracts has shown that in different animals the purine enzymes are differently distributed; the present experiments, in which purines were given either parenterally (in animals) or by the mouth (in man) support the view that the metabolic history of the purines varies in different animals. The difficulty man has in oxidising uric acid, as shown by its reappearance in the urine after parenteral administration, fits in with the examination of tissue extracts, in which no uricolytic enzyme is found in human tissues. On the other hand, a large proportion of the uric acid introduced into the rabbit does not reappear as such. After injection of adenine in dogs and rabbits, there is a relatively large output of unaltered adenine, and but little uric acid or allantoin. If guanine is given, there is a larger output of allantoin, xanthine, and uric acid. Guamase is more widespread in rabbit and dog tissues than adenase. In the pig, uric acid is not the chief end-product of purine metabolism. In man, the protocols given emphasise the fact that all the ordinary purines lead to an increase of exogenous uric acid, with but little influence on the elimination of purine bases in the urine. W. D. H.

Cleavage of Histidine in the Organism of the Dog. ERIC ABDERHALDEN, HANS EINEBECK, and JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, 68, 395—399. Compare Abstr., 1909, ii, 906).—Intravenous administration of histidine in a dog does not lead to increase in the excretion of allantoin in the urine. If given by the mouth, the increase of allantoin is very slight, and sometimes absent. Very little of the histidine given (0.4 out of 20 grams) is recoverable as such in the urine. Nucleic acid raises the allantoin excreted. W. D. H.

Influence of the Removal of Fragments of the Gastro-intestinal Tract on the Character of Nitrogen Metabolism. III. **The Excision of the Stomach.** A. CARREL, GUSTAVE M. MEYER, and PHILIP A. LEVINE (*Amer. J. Physiol.*, 1910, 23, 369—380. Compare this vol. ii, 323).—Two dogs were operated on, and in one of them the extirpation of the stomach was quite complete. Before the tenth week there is high nitrogen retention, probably because the pancreatic and intestinal secretions are interfered with, but after this date no nitrogen retention occurs. Parenterally introduced protein was completely retained in the organism. W. D. H.

Imbibition of the Intestinal Mucous Membrane with Sodium Chloride and Sulphate Solutions of Different Concentrations. G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1910, 27, 516—529).—The present experiments deal with sodium sulphate; they support Loeper's conclusions, and show that the salt has an inhibitory influence on imbibition, but this is regarded as a secondary effect; the opinion is held that it is the ions working on the intestinal muscle which explains the purgative action of the salt. W. D. H.

The Influence of Sugar on the Permeability of the Intestinal Membrane. ERNST MAYERHOFFER and ERNST STEIN (*Biochem. Zeitsch.*, 1910, 27, 376—384).—The permeability of the intestinal mucous membrane of rabbits, removed after death, is increased towards normal ammonium chloride solution by placing the membrane in a 5% solution of dextrose. Supposing the same to be true *in vivo*, cases of dyspepsia due to excess of sugar are explicable. W. D. H.

The Fate of Sucrose after Parenteral Introduction in Animals. LAFAYETTE B. MENDEL and ISRAEL S. KLEINER (*Amer. J. Physiol.*, 1910, 26, 396—406).—When sucrose is introduced intraperitoneally or subcutaneously into dogs and cats in doses of 1—2 grams per kilo. of body-weight, about 65% is recovered in the urine, and a reducing fermentable substance is also sometimes present. The excretion begins within a few minutes, and is usually completed in thirty-six hours. The actual figure, however, varies with different conditions (fasting, pregnancy, etc.). Sucrase was not found in the blood; nevertheless, as Abderhalden and Brahm showed, there is a possibility of sucrose digestion in the blood, which may account for the disappearance of part of the sugar. W. D. H.

The Value of Beer-extract and Beer in the Human and Animal Organism. WILHELM VÖLTZ, RUDOLF FÖRSTER, and AUGUST BACHDREXEL (*Pflüger's Archiv*, 1910, 134, 133—258).—The dry residue of beer extract elevates the absorption of non-nitrogenous material, especially fat. Approximately 40% of the nitrogenous substance is absorbed. Observations both on men and dogs are given, and deductions as to its nutritive value coincide in the main with those of Atwater and Benedict. Observations with toxic doses are also given. The general trend of the article is a defence of the use of alcohol in moderation, especially in the form of beer. W. D. H.

Digestibility of Bleached Flour. ELBERT W. ROCKWOOD (*J. Biol. Chem.*, 1910, 8, 327—340).—Experiments on the artificial digestion of unbleached flour, as compared with specimens of the same flour bleached with nitrogen peroxide, show no loss of digestibility, and in some cases the bleached specimens digested more rapidly than the unbleached. W. D. H.

The Value of the Cleavage Products of Protein in the Animal Organism. XVI. EMIL ABDERHALDEN and AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, 68, 416—420. Compare this vol., ii, 877).—A dog was fed exclusively on the cleavage products of flesh without admixture of fat or carbohydrate. The preparation used was "ereptone," made from meat by the successive action of gastric, pancreatic, and intestinal juices. Vomiting and diarrhoea were to some extent overcome by giving the food carefully in small doses through a gastric fistula. The animal gained in weight, and put on flesh. The conclusions drawn by Voit and Zisterer (this vol., ii, 425) from somewhat similar experiments are criticised. W. D. H.

The Temperature-coefficient of Cytolysis in the Unfertilised Egg of the Sea-Urchin. A. R. MOORE (*Quart. J. exper. Physiol.*, 1910, 3, 257—260).—The temperature-coefficient for the process of cytolysis of sea-urchin eggs in sea-water was found to be about 200 for a difference in temperature of 10°. The same figure was calculated from Gros's data for hæmolysis. W. D. H.

Differentiation of Proteins of Closely Related Species by the Precipitin Reaction. D. A. WELSH and H. G. CHAPMAN (*J. Hygiene*, 1910, 10, 177—184).—It is possible to distinguish heterologous proteins of closely related species by precipitin interactions arranged with regard to the fact that in the conditions of experiment the weight of precipitates is proportional to the weight of the anti-serum employed. This is illustrated by experiments with the albumin prepared from different birds' eggs. The experiments support the authors' previously expressed view that the anti-serum is the main source of the precipitate in the precipitin reaction. W. D. H.

Chemico-Physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 162—169. Compare this vol., ii, 143).—The authors have

investigated the influence of various chlorides (those of sodium, potassium, calcium, and magnesium) and of various sodium salts (chloride, nitrate, acetate, sulphate, and tartrate) on the imbibition of water by the crystalline lens. Solutions of the following concentrations were employed: $N/5$, $N/50$, $N/100$, $N/150$, $N/200$. In all cases the imbibition was less than that which occurs when the lens is immersed in pure water, and the decrease was greater in the case of the $N/5$ solutions than with the weaker ones. As regards the specific actions of the different ions (for the elucidation of which the results with the strongest solutions are the most trustworthy), it appears that the bivalent cations (magnesium and calcium) diminish the imbibition more than the univalent cations (sodium and potassium), although there are considerable irregularities, which are still more pronounced in the case of the different anions.

R. V. S.

Heart Metabolism. I. Metabolic Investigations of the Surviving Warm-blooded Heart. ERWIN KONDE (*Zeitsch. physiol. Chem.*, 1910, 68, 181—235).—Previous work on the isolated mammalian heart, such as that by Locke and Rosenheim on its capacity to utilise sugar, or of Barcroft and Dixon on its gaseous metabolism, is on the whole confirmed; the special feature of the apparatus here used is that simultaneously means are adopted for measuring the work of the heart. The metabolic changes run parallel to the amount of work done. In the presence of sugar, not only is sugar burnt, but often constituents in the heart itself (reserve material) are burnt also, and thus leads to the production of carbon dioxide. When sugar or other nutritive material is absent, those reserve materials are alone utilisable; these probably originate from fat and protein, and the hypothesis is put forward that the heart forms a sort of internal secretion in which glycolysis occurs.

W. D. H.

The Injury to the Heart's Activity Produced by Glyoxylic Acid. R. H. KAHN and EMIL STARKENSTEIN (*Pflüger's Archiv*, 1910, 133, 579—597).—The bulk of this paper has but little chemical interest. Cardiac activity was studied by the cardio-electrogram, and the causes of pulsus alternans are discussed. In glyoxylic acid poisoning, this symptom is pronounced.

W. D. H.

Union Relationships of Heart Muscle and Digitalis. B. SCHLIOMENSUN (*Arch. exp. Path. Pharm.*, 1910, 63, 294—302).—From the hearts of men and animals a group of substances can be isolated, namely, the alcohol-soluble phosphatides, which appear to have a special capacity to combine with the active material in digitalis. The corresponding fractions from the skeletal muscles and liver do not possess this property. It is not possible at present to say what are the definite chemical substance or substances that participate in this specific reaction.

W. D. H.

The Formation in the Animal Body of l - β -Hydroxybutyric Acid by the Reduction of Acetoacetic Acid. HENRY D. DAEIN (*J. Biol. Chem.*, 1910, 8, 97—104).—The liver contains not only an

oxylase which converts β -hydroxybutyric acid into acetoacetic acid, but also a reductase which produces the reverse change. The view taken of l - β -hydroxybutyric acid acidosis is that its main underlying cause is defective catabolism of acetoacetic acid. The conclusions are supported by experiments. The question is discussed whether the phenomena are due to the reversible action of one enzyme, or to the antagonistic action of two enzymes. The latter hypothesis fits in best with the facts.

W. D. H.

The Degradation of Carboxylic Acids in the Animal Body.
XII. A New Method of Formation of β -Hydroxybutyric Acid in the Animal Body. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, 27, 474—490. Compare this vol., ii, 794, 795).—In experiments on perfusion of the dog's liver with ox-blood a fair amount of l - β -hydroxybutyric acid is formed, in most cases without the addition to the perfusing liquid of any substance which yields acetoacetic acid. If sodium acetoacetate is added to the perfusing blood, a large amount disappears, and from 42 to 62% of this is accounted for by the l - β -hydroxybutyric acid formed. If sodium butyrate, or especially isovalerate, is added, there is a large formation of both acetoacetic and β -hydroxybutyric acids. Similar results were obtained in experiments with pounded liver substance. The agent which converts acetoacetic acid into l - β -hydroxybutyric acid is termed *keto-reductase*.

W. D. H.

The Decomposition of Acetoacetic Acid by Enzymes of the Liver. II. ALFRED J. WAKEMAN and HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 8, 105—108).—Further facts are given in relation to the liver reductase; the primary product of its action on acetoacetic acid is not acetic acid, but l - β -hydroxybutyric acid.

W. D. H.

Uric Acid Metabolism in Dogs. H. ACKROYD (*Bio.-Chem. J.*, 1910, 5, 217—224).—The liver of dogs when perfused with normal saline solution produces a small quantity of allantoin. When sodium urate is added to the perfusion fluid, a part of it is destroyed; part only of this is recovered as allantoin; no uric acid could be isolated. The dog's liver has not the power to destroy allantoin.

W. D. H.

The Formation of Uramido-acids in the Organism. I. FRITZ LIPPEICH (*Zeitsch. physiol. Chem.*, 1910, 68, 277—292).—The formation of uramido-acids in the body is important from the standpoint of uric acid formation, and former work on the question is quoted at length. The present experiments on the action of the dog's liver in the formation of such acids gave negative results.

W. D. H.

Liver Pigments of Invertebrates. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1910, 23, 56—59).—From the liver of invertebrates (molluscs being mainly used), two pigments were obtained, one soluble in water, the other in chloroform or alcohol. The former is rich in iron, and gives a continuous spectrum, the latter poor in, or free from, iron gives absorption bands. The same pigments are stated to be also obtainable from the vertebrate liver.

W. D. H.

Study of Autolysis by Physico-chemical Methods. II. ROBERT L. BENSON and H. GIDEON WELLS (*J. Biol. Chem.*, 1910, 8, 61-67. Compare *ibid.*, 1907, 3, 35).—Autolysis is usually measured by the change in the amount of nitrogen contained in forms coagulable and not coagulable by heat, but it is shown by experiments with dog's liver, blood-serum, and blood that autolysis can be followed much more satisfactorily by freezing-point determinations supplemented by electrical conductivity measurements. Toluene was found to be the most satisfactory antiseptic in these experiments.

In agreement with Baer and Loeb (*Abstr.*, 1905, ii, 734), the authors find that the inhibiting effect of serum on autolysis (the effect of dog serum on the autolysis of dog liver was observed) is scarcely affected by heating the serum at 85° or 95° for thirty minutes. In other cases, the inhibiting effect of serum appears to be diminished by heating, but there seems to be some discrepancy in the results obtained when the autolytic changes are measured by physical or chemical means, and when they are measured by the histological changes taking place in the cells. G. S.

The Occurrence of Free Guanosine in the Pancreas. PHOEBUS A. LEVENE and WALTER A. JACOBS (*Biochem. Zeitsch.*, 1910, 26, 127-130).—The separation of guanylic acid from the pancreas was found to be difficult, owing to the presence of guanosine, which is regarded as being in the free stato. In fact it is sometimes more abundant than the acid. W. D. H.

Ethyl Acetate Extracts of Organs and their Behaviour in Autolysis. IV. and V. KENRO KONDO (*Biochem. Zeitsch.*, 1910, 27, 427-435, 436-441. Compare this vol., ii, 791).—The present experiments with kidney, spleen, and blood were carried out in the same way as in previous work on the liver. The results with kidney and spleen (to some extent) were very similar, and there appears to be present in these organs substances other than cholesterol containing hydroxyl groups, the quantity of which increases in the warm. In the case of the blood, there was no evidence of any enzyme either in the corpuscles or plasma capable of splitting cholesterol esters. The acetyl number remains unchanged after autolysis. This is not due to the presence of an inhibiting agent, for the increase occurs when liver extract is added. W. D. H.

Formation of Oxalic Acid in the Organism. HERMANN JASTROWITZ (*Biochem. Zeitsch.*, 1910, 28, 34-47).—Oxalic acid can arise from uric acid, aminodicarboxylic acids, and carbohydrates. In intermediate metabolism, it is formed especially in the spleen, and probably also in the liver and muscles (in dogs). In anomalies of nuclein metabolism (gout, leucæmia), increased oxalic acid formation occurs very seldom, but it may occur in diabetes. W. D. H.

Metabolic Disturbances after the Extirpation of both Suprarenal Glands. OSWALD SCHWABZ (*Pflüger's Archiv*, 1910, 134, 259-288).—The animals used were rats; when both the suprarenals

are removed, the hepatic glycogen is much reduced or disappears entirely; this is regarded, not as due to general marasmus, but as a specific effect of the operation; when then fed on bread, glycosuria is produced; with feeding on pure dextrose, the glycogen returns in some measure to the liver. The administration of lævulose leads neither to glycogen formation nor to lævulosuria; it is apparently completely utilised in the body; feeding on sucrose leads to glycogen formation in virtue of its dextrose component; after feeding on starch, alanine, or aspartic acid, the liver is free from glycogen. Phloridzin is highly toxic to these animals; it produces glycosuria; they are also sensitive to adrenaline injections. A sugar mobilising function is assigned to adrenaline.

W. D. H.

Toxic Action of Compound on Isolated Muscle Regarded as a Chemical Change. VICTOR H. VELEY (*Quart. J. Exper. Physiol.*, 1910, 3, 233—249).—From the experiments previously recorded by the author (mainly in conjunction with Waller, this vol., ii, 55, 228, 331, 524), the conclusion is drawn that living muscular tissue behaves as if it contained, not only proteins as such, but even their products of decomposition or hydrolysis, or, in other words, the living muscle behaves like a lifeless chemical reagent; the results obtained are not greatly inferior in accuracy to those obtained in reactions between highly refined chemical compounds under rigid physical conditions.

W. D. H.

The Quantitative Relations of Diastase in Different Organs of Different Animals. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, 27, 385—396).—In estimating the diastase, Wohlgemuth's method and notation are employed. The pancreas, spleen, liver, blood, kidney, and other organs of various mammals, birds, fishes, and amphibians were investigated. The pancreas in all cases contains most diastase; the blood and liver generally come next; in rats on a starch diet, the diastase value of the pancreas rises from 300 to 400-fold.

W. D. H.

Presence of Glycuronic Derivatives in Beef Bouillon. LÉON GRIMBERT and E. TURPAUD (*J. Pharm. Chim.*, 1910, [vii], 2, 289—292).—The presence of reducing substances in aqueous extracts of beef has long been known, and the action has been variously ascribed to dextrose, maltose, isomaltose, pentoses, or glycuronic acid.

The author finds that bouillon, defaecated by mercuric nitrate solution, or boiled with hydrochloric acid, yields with phenylhydrazine a mixture of phenylglucosazone and phenylglycosazone (Grimbert and Bernier, this vol., ii, 163). Glycuronic derivatives can also be detected by Tollens' reagent in bouillon defaecated by mercuric acetate, and from which the dextrose has been eliminated by the action of *Bacterium coli*.

T. A. H.

Manganese of the Tissues of Lower Animals. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1910, 8, 237—250. Compare Abstr., 1907, ii, 567).—Analyses of the amount of manganese in the different parts of various mussels are given. It is not regarded as merely adventitious; it is constantly present, and in spite of the small amount

present in the muscular tissue (which has a low order of activity in these animals), probably plays a rôle in respiration. In lakes poor in manganese (and poor also in the *Crenothrix* and diatoms which contain large amounts of manganese and form the food of the mussels), mussels cannot live.

W. D. H.

Alcohol Oxydase in Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1910, 28, 145—168).—*Alcohol-oxydase* (alcoholase) is an enzyme which acts chiefly on ethyl alcohol, and converts it into acetic acid by absorption of molecular oxygen; aldehyde is an intermediate product; it also oxidises aldehyde directly. The enzyme does not decrease in amount in the tissues one or two days after death. It is most abundant in the liver, especially of the horse; the amount in human liver is relatively small; the kidneys also contain it, but the amount in other organs is very small. It acts neither in acid nor in strongly alkaline media; it acts best in faintly alkaline media. Addition of spleen to the liver increases the effect. Hydrogen peroxide has no effect.

W. D. H.

Further Investigations on the Use of Silk Peptone for the Detection of Peptolytic Enzymes. EMIL ABDERHALDEN and EUGEN STEINECK (*Zeitsch. physiol. Chem.*, 1910, 68, 312—316).—Details are given in regard to the best methods for obtaining silk peptone. Slices of organs (for instance, kidneys) placed in the peptone solution become, if a peptolytic enzyme is present, covered with tyrosine crystals. Whether healthy and pathological organs vary in this direction is to be further investigated. In the developing chick, peptolytic enzymes appear in the tissues at seventh to eighth day of incubation; in the pig embryo, in nearly all the tissues after the thirty-seventh day of development.

W. D. H.

Enzymatic Acceleration of Cannizzaro's Aldehyde Transformation by Tissue Extracts. I. JAKOB PARNAS (*Biochem. Zeitsch.*, 1910, 28, 274—294).—Animal tissues usually contain both fatty acid and the corresponding alcohol, and it is suggested that these are both derived from aldehyde by the Cannizzaro transformation. The liver, but not the lungs, contains a soluble ferment which accelerates this transformation, so that it takes place with aldehydes which otherwise tend to undergo aldol condensation. Quantitative production of the corresponding acid and alcohol was obtained from *n*- and isovaleraldehydes, isobutaldehyde, and propaldehyde, also from heptaldehyde after three hours' action of pig or ox liver. Benzaldehyde yielded a small quantity of alcohol; salicylaldehyde was not attacked. The name *aldehydemutase* is proposed for the enzyme.

E. F. A.

Enterolipase. B. C. P. JANSSEN (*Zeitsch. physiol. Chem.*, 1910, 68, 400—415).—As Lombroso showed, a mixture of bile and oleic acid stimulates the secretion in the intestine of a juice rich in lipase. Oleic acid alone has no such effect. Bile alone has not so great an effect as the mixture. These experiments were made with intestinal

loops. *In vitro*, the addition of bile increases the lipolytic action of the juice. Soap solution causes the secretion of a feebly lipolytic juice; *in vitro*, soap inhibits lipolytic action, but a small addition of alkali increases it. The addition of bile acids to bile increases its power of stimulating the secretion of lipase, and the effect of the mixture of bile and oleic acid is probably due to the bile acids. The group in the bile acid molecule to which this is due is to be the subject of renewed investigation.

W. D. H.

Occurrence of Serine in Human Perspiration. GUSTAV EMBDEN and HERMANN TACHAU (*Biochem. Zeitsch.*, 1910, 28, 230—236).—Hitherto only two nitrogenous substances, carbamide and ammonia, have been isolated from perspiration. From fresh perspiration, fairly large quantities of serine are now isolated by means of β -naphthalene-sulphonic acid. This method is advantageous in separating serine from the mixture of protein decomposition products obtained by acid hydrolysis.

E. F. A.

The Production of Glycosuria in Relation to the Activity of the Pancreas. IVOR L. TUCKER (*J. Physiol.*, 1910, 41, 88—144).—Glycosuria due to anæsthesia and operation is probably not influenced by the pancreatic factor; neither is there evidence that the carbohydrate in the diet stimulates the pancreas to an increase in its internal secretion. Glycosuria following fistula or ligature of the thoracic duct is probably due to the anæsthetic employed and to disturbance of nerves, but as the internal secretion of the pancreas finds its way into the circulation by this duct, that may possibly be a subsidiary factor. The glycosuria associated with morphine and ether narcosis is the result of the rapid production of sugar from hepatic glycogen, other carbohydrates in the body, and also from fat. The sugar in the blood of cats exhibiting experimental glycosuria has a reducing power equal to that of dextrose.

W. D. H.

Nature of Bence-Jones Protein. OWEN T. WILLIAMS (*Bio.-Chem. J.*, 1910, 5, 225—229).—The protein was obtained in the urine of a case of myeloma; it is shown that it varies in composition from time to time even in the same case, and probably the true explanation lies in the fact that in the disintegration of bones and tendons, chondro-mucins are liberated, which are more or less broken up, and thus excreted differently according to the stage of the disease. The protein in the present case gave the typical reactions of the Bence-Jones protein. It resembles mucoid in that it contains a carbohydrate radicle and a high percentage of sulphur. The latter, however, varies, and when it sinks the amount of ethereal sulphate in the urine rises.

W. D. H.

Diastase in the Blood and Urine of Rabbits. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, 28, 23—28).—In experimental nephritis in rabbits, the diastase in the urine sinks; this is regarded as due to lessened functional activity of the kidney cells, and the decrease is greatest in cases where the injury is greatest. The rise of diastase in

the blood which accompanies this is regarded as due to defective elimination by the kidneys.

W. D. H.

Metabolism in Addison's Disease. H. BEUTENMÜLLER and FELICITAS STOLTZENBERG (*Biochem. Zeitsch.*, 1910, 28, 138—144).—In the case of Addison's disease investigated there was no important departure from the normal in nitrogen metabolism; on an abundant diet, the patient retained nitrogen; the administration of adrenal tablets had no effect.

W. D. H.

The Excretion of Creatine in Diabetes. R. A. KRAUSE (*Quart. J. Exper. Physiol.*, 1910, 3, 289—296).—A full account of experiments already published as a preliminary communication (see Krause and Cramer, this vol., ii, 793).

W. D. H.

Prophylaxis in Malaria. Action of Small Continuous Doses of Quinine on the Development of the Animal Organism and its Application in Infectious Disease. ALBERT GRAZIANI (*Arch. Hygiene*, 1910, 73, 39—80).—Injection of quinine hydrochloride for one hundred days in doses of 0.005 gram per kilo. of body-weight in young rabbits and guinea-pigs delays growth, and in adult animals lessens their weight. There is no change in the corpuscles or hæmoglobin of the blood; the bactericidal power of the lungs or of the serum is unaltered; so also are the opsonic index and the agglutinating action of the blood in reference to typhoid bacilli; in fact, in most cases the immunising power of the blood is diminished. The animals which had received quinine are much less resistant towards infection (typhoid, anthrax, cholera, pneumonia) than the control animals. Observations on the blood of man show the same results, and the conclusion is drawn that the same loss of resistance occurs in man also.

W. D. H.

Atoxyl. IV. FERDINAND BLUMENTHAL (*Biochem. Zeitsch.*, 1910, 28, 91—96. Compare Abstr., 1909, ii, 255).—The use of atoxyl preparations and of its various iodine and bromine derivatives in syphilis is suggested. The present experiments are mainly on animals to discover the relative toxicity of these compounds; the silver salts are less poisonous than those of mercury.

W. D. H.

Absorption of Hydrogen Chloride by Animals. KARL B. LEHMANN and ARTHUR BURCK (*Arch. Hygiene*, 1910, 72, 343—357).—In tracheotomised rabbits, the amount of hydrogen chloride absorbed in the first hour varied between 58 and 80% of the amount inspired; higher figures were obtained when the gas was given through the nose. The absorption increases with the depth of respiration. In the second hour there was no marked falling off in the rate of absorption; experiments lasting more than two hours were not made.

W. D. H.

Absorption of Chloroform, Carbon Tetrachloride, and Tetrachloroethane in Animals and Man. KARL B. LEHMANN and HASEGAWA (*Arch. Hygiene*, 1910, 72, 327—342).—The experi-

ments on two men were carried out by estimating the chloroform in the inspired and expired air, the difference giving the amount absorbed. In periods of five to ten minutes from 53 to 73% of the chloroform given was absorbed. In experiments for longer periods, the amount absorbed was greatest in the first five minutes, and then gradually declined. In rabbits the same falling off was noticed, but the total absorption was less than in man. Administration was either made by the nose or by the tracheal tube, but the method made no difference. Similar figures (in rabbits) were obtained with carbon tetrachloride and tetrachloroethane.

W. D. H.

Influence of Gases on the Organism. XV. Hydrogen Arsenide. L. O. DUBITZKI (*Arch. Hygiene*, 1910, 73, 1—38).—This gas was estimated in the air volumetrically either by calcium chloride, silver nitrate, or potassium iodate. In cats, 0.005% is fatal in sixty to ninety minutes, 0.004% in three hours. A prominent symptom is hemolysis leading to hæmoglobinuria. The absolute fatal dose varies from 8.7 to 13.7 milligrams.

W. D. H.

Action of Radium Emanations on the Development of Animal Eggs. II. OSCAR HERTWIG (*Sitzungsber. K. Akad. Wiss., Berlin*, 1910, 39, 751—771).—Experiments on various eggs confirm the author's previous conclusions. The main interest of the paper relates to the action of the radium emanations on the sperm of the frog. After exposures varying from five minutes to twelve hours, the spermatozoa becomes more or less altered, but the nucleus is the most affected. These spermatozoa are still capable of fertilising the eggs, although development is slow in cases of long exposure and abnormal embryos are formed. This is regarded as an additional proof that the nuclear substance is the most important part of the male cell in fertilisation.

W. D. H.

Action of Radium Bromide on the Skin of the Rabbit's Ear. J. O. WAKELIN BARRATT (*Quart. J. exper. Physiol.*, 1910, 3, 261—270).—A disk of radium bromide placed on the ear of the rabbit produced a ring of pigmentation corresponding with the edge of the disk. Within the ring more or less depigmentation occurred. The deposit of pigment took place chiefly in the epidermis. In albino rabbits and with human skin no such effects were observed.

W. D. H.

The Pharmacological Action of Uranium. D. E. JACKSON (*Amer. J. Physiol.*, 1910, 26, 381—395).—The action of uranium is generally believed to resemble that of cyanides, but there are many points of difference. Intravenously administered as the sodium uranium tartrate there is no increase in the flow of lymph from the thoracic duct even in lethal doses. The rise of arterial pressure is much more pronounced than that produced by cyanides, and the stimulating action on respiration is less marked. Blood coagulation is prevented, probably by union of the metal with one or more of the protein factors in the process. Further, there is no change in the hæmoglobin. Cyanides binder the guaiacum reaction with extract of potato peelings; uranium does not.

W. D. H.

Behaviour of Iodoso-, Iodoxy-, and Iodonium Compounds in the Animal Organism. II. Behaviour of Iodoxybenzene. RICCARDO LUZZATTO and G. SATTA (*Arch. Farm. sper. Sci.*, 1910, 9, 241—253. Compare this vol. ii, 433).—Even in quantities five times greater than the toxic dose of iodosobenzene, iodoxybenzene does not cause death in dogs, rabbits or frogs. The effects it produces are similar in kind to those of the former substance, but its action is much weaker and slower. It is converted in the organism into iodo-benzene, for iodophenylmercapturic acid can be isolated from the urine, and its lower toxicity is probably due to the fact that this reduction occurs more easily than in the case of iodosobenzene. Iodoxybenzene does not exhibit any curare-like action on frogs.

R. V. S.

The Behaviour of β -p-Hydroxyphenyl- α -lactic Acid and p-Hydroxyphenylpyruvic Acid in the Surviving Liver. ERNST SCHMITZ (*Biochem. Zeitsch.*, 1910, 28, 117—120).—Neubauer and Falta have shown that those aromatic substances the ring of which is easily burnt in the body are excreted in alcaptonuria as homogentisic acid, whereas those which are not, or only with difficulty, broken up have no such influence on the excretion of homogentisic acid. Embden, Salomon, and Schmidt have shown that the former group leads in the isolated liver to formation of acetoacetic acid, whereas the latter does not. In the present experiments on liver perfusion this is confirmed; β -p-hydroxyphenyl- α -lactic acid does not yield homogentisic acid, and leads to a negligible formation of acetone substances in the liver; p-hydroxyphenylpyruvic acid leads to homogentisic acid formation in alcaptonurics and to an abundant formation of acetone substances in the surviving liver.

W. D. H.

Chemical and Physiological Properties of Triphenylstibine Sulphide. Behaviour of this Substance in the Animal Body. LUDWIG KAUFMANN (*Biochem. Zeitsch.*, 1910, 28, 67—88, 86—90. Compare Abstr., 1908, i, 1031).—Triphenylstibine sulphide has the power to produce the evolution of oxygen from hydrogen peroxide and other peroxides; the sulphur is split off and oxidised to sulphuric acid, whilst the residue is oxidised to antimony oxide or hydroxide and precipitated as sulphate by the sulphuric acid. The reaction runs quantitatively at a temperature of 36—37°. The sulphite is one hundred times more active than ordinary sulphur.

The therapeutic use of the sulphide in cases (for instance, of skin disease) where sulphur is usually employed appears from a few preliminary observations and experiments to be justifiable.

W. D. H.

Chemical Structure and Sympathomimetic Action of Amines. GEORGE BARGER and HENRY H. DALE (*J. Physiol.*, 1910, 41, 19—59).—The action of adrenaline on the sympathetic is termed sympathomimetic, and is also shown by a large series of amines, the simplest being primary fatty amines. The action increases with approximation to adrenaline structure. The amines active in this way

are primary or secondary; the quaternary amines corresponding with the aromatic members of the series have an action like that of nicotine. The optimum carbon skeleton for sympathomimetic activity consists of a benzene ring with a side-chain of two carbon atoms, the terminal one bearing the amino-group. Another optimum condition is the presence of two phenolic hydroxyls in the 3:4 position relative to the side-chain; when these are present, an alcoholic hydroxyl still further intensifies the activity. A phenolic hydroxyl in the 1 position does not increase the activity. Catechol has no such activity. The methyl-amino-group, including adrenaline, reproduces inhibitory sympathetic effects more readily than motor effects; the opposite is true for the primary amines of the same series. Instability and activity show no parallelism in the series.

W. D. H.

The Fate of *p*-Hydroxyphenylethylamine in the Organism. ARTHUR J. EWINS and PATRICK P. LAIDLAW (*J. Physiol.*, 1910, 41, 78—87).—This amine is converted in part in the body into *p*-hydroxyphenylacetic acid; the surviving liver can effect this change, so also can the plain muscle of the uterus, but not that of the lung vessels. The isolated heart causes complete destruction of the amine. The amine is less readily converted into hydroxyphenylacetic acid than the primary amine, and hordenine, the tertiary base, still less readily than the secondary base.

W. D. H.

The Behaviour of Veronal (Sodium Veronal) in the Animal Body, after One Administration, and in the Chronic Condition. C. BACHEM (*Arch. exp. Path. Pharm.*, 1910, 63, 228—241).—After the subcutaneous injection of small doses of veronal, about 90% appears in the urine; in larger doses this sinks to 45—50% whether the drug is given in one or successive doses. The faeces contain only a small quantity, so about half is destroyed in the body, how or why is unknown. Small doses do not influence the well-being of the animals used. After three days, only small amounts are still found in the urine and organs. Its affinity for brain tissue is doubtless related to its narcotic properties. Even after large doses, a small fraction only is found in the stomach some hours later. In acute poisoning, the stomach must therefore be washed out early if it is to be of any avail.

W. D. H.

The Prophylactic Action of Atropine in Immediate Anaphylaxis of Guinea Pigs. III. JOHN AUER (*Amer. J. Physiol.*, 1910, 26, 439—452).—Guinea pigs sensitised by the subcutaneous injection of 1 to 2 c.c. of horse-serum reach their maximum sensitiveness about the ninth week, and this is then maintained for at least twenty-three weeks (the longest interval tested). Atropine was used as a prophylactic, as the symptoms of anaphylaxis are mainly due to contraction of bronchial muscles. Experimentally, atropine was found to be of distinct therapeutic utility. Without atropine, the death rate was 75%, with it only 28%.

W. D. H.

The Clinical Application of Ergotamine (Tyramine). ALFRED CLARK (*Bio.-Chem. J.*, 1910, 5, 236—242).—Tyramine given by the

mouth to a healthy subject in doses of 30 to 100 mg. causes a slight rise of blood-pressure which lasts some hours. When injected hypodermically (20 to 50 mg.), the rise is rapid and well marked, lasting about twenty minutes. When similarly given in cases of "shock," the blood-pressure rises slightly.

W. D. H.

Action of Curarine and Allied Substances. RUDOLF BOENIG (Arch. exp. Path. Pharm., 1910, 63, 177—227).—The direct excitability of skeletal muscle (frog) to induction shocks remains unaltered even by large doses of curarine, but the excitability varies in different parts. Towards condenser discharges, the effects are variable, as also they are in normal muscles. Muscles can easily be poisoned with curarine by immersing them in a solution of the drug. The great toxicity of the drug comes out when it is compared with other ammonium derivatives; the following relative figures are given: Choline, 0.35; tetraethylammonium, 0.125; trimethylethylammonium, 0.015; neurine, 0.012; tetramethylammonium, 0.005; muscarine, 0.0025; trimethylvaleryl ammonium (valearine), 0.001; curarine, 0.00001.

W. D. H.

Elementary Action of Digitalis Substances. RUDOLF MAGNUS and (Miss) S. C. M. SOWTON (Arch. exp. Path. Pharm., 1910, 63, 255—262).—Observations by the authors confirm Straub's views on the action of the digitalis group. The increased activity of the heart can be shown, not only in the intact animal, but also on the isolated heart. Illustrative experiments on the effect of strophanthin are given in full.

W. D. H.

The Concentration of Ammonia in the Blood of Cats and Dogs necessary to Produce Ammonia Tetany. CLARA JACOBSON (Amer. J. Physiol., 1910, 26, 407—412).—Ammonium carbonate was injected intravenously, and the concentration in the blood found necessary to produce tetany is identical with the concentration of ammonia in the blood when tetany occurs as a result of removal of the parathyroids. In the latter condition the liver is depressed in its power to destroy ammonia.

W. D. H.

Antimony Poisoning in Compositors. P. SCHRUMPF and B. ZABEL (Arch. exp. Path. Pharm., 1910, 63, 242—254).—Various symptoms presented by compositors could not be attributed to lead poisoning, but are due to antimony; the blood conditions underlying this are a slight leucocytosis, but a great excess of eosinophile cells. Similar conditions can be produced artificially by antimony in rabbits. No drug treatment is suggested; mere cessation of work in the men, or cessation of antimony dosage in animals, leads rapidly to a return to normal conditions.

W. D. H.

The Comparative Toxicity of Theobromine and Caffeine as Measured by their Direct Effect upon the Contractility of Isolated Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (Proc. Roy. Soc., 1910, 82, B, 568—574).—Caffeine produces con-

tracture and finally abolition of contraction in muscle. With caffeotannic acid the admixture with tannic acid retards the change. Theobromine causes a similar effect, its toxic value compared with that of caffeine being 1·7:1 for equal molecules, or 1·8:1 for equal weights. The introduction of the methyl group into theobromine to form caffeine lowers the toxicity, a result converse to that found in certain other organic compounds. Experiments are also recorded with extracts of tea and coffee; "caffeine-free" coffee has but little action.

W. D. H.

The Relationship of Surface-tension to the Union of Toxin and Anti-toxin. AMILCARE BERTOLINI (*Biochem. Zeitsch.*, 1910, 28, 60—66).—Traube stated that toxins in opposition to anti-toxins lower the surface-tension, and that the union of toxin and anti-toxin has a still greater effect than the toxin. The present investigations made with diphtheria and tetanus toxin and anti-toxin do not confirm this view. The union has no effect on surface-tension as tested by Traube's stalagmometer.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Apparatus for Collecting and Measuring the Gases Evolved During Fermentation. ARTHUR HARDEN, J. THOMPSON, and WILLIAM J. YOUNG (*Bio.-Chem. J.*, 1910, 5, 230—235).—In measuring the total quantity and rate of evolution of gases evolved during fermentation, it is essential to keep the pressure in the flask as nearly constant as possible throughout the experiments.

Two forms of apparatus devised and used by the authors for this purpose are fully described with diagrams.

W. D. H.

Influence of the Mineral Constituents of Nutritive Solutions on the Development of *Azotobacter*. (Mme.) H. KRZEMIENIEWSKA (*Bul. Acad. Sci. Cracow*, 1910, B, 376—413).—Potassium, calcium, magnesium, phosphorus, and sulphur are all essential to the development of *Azotobacter*. Under the conditions of the experiments, the minimum amounts required for the normal consumption of 1 gram of dextrose were as follows: K, 0·38; Ca, 0·36; Mg, 0·35; P, 2·46; and S, more than 0·49 mg. Deficiency of any essential mineral constituent of the nutritive solution results in the less economical utilisation of the dextrose, and consequently less nitrogen is fixed per gram of dextrose. The organisms leaves off increasing, whilst the respiration of the existing cells goes on.

The addition of potassium, sodium, and magnesium compounds above certain limits acts injuriously on *Azotobacter*. The injurious effect is diminished or prevented by addition of calcium salts. Addition of magnesium salts lessens the injurious action of excessive amounts of potassium and sodium.

N. H. J. M.

Assimilation of Nitrogen by Certain Nitrogen-fixing Bacteria in the Soil. W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1910, B, 82, 627—629. Compare *ibid.*, 81, 287).—Culture solutions inoculated respectively with pure cultures of *Azotobacter* from garden soil, and *Pseudomonas* from bean and clover nodules and with both organisms together, showed that whilst *Azotobacter* alone fixed 2.19 mg. and *Pseudomonas* alone 2.30 mg. of nitrogen per unit of carbohydrate, the two organisms together fixed 4.51 mg. per unit of carbohydrate.

Further experiments are described in which garden soil (5 oz.), both without and with lime, was inoculated from an extract of soil which had been sterilised and then inoculated with *Azotobacter* and *Pseudomonas* so as to accustom the organisms to soil conditions. In ten days the mixed culture in limed soil gave an increase of 35 mg. of nitrogen, and in the unlined soil an increase of 25 mg. The amount of nitrogen introduced by the culture itself was 6 mg. N. H. J. M.

Some Factors Concerned in the Fixation of Nitrogen by *Azotobacter*. CONRAD HOFFMANN and B. W. HAMMER (*Centr. Bakt. Par.*, 1910, ii, 28, 127—139).—Experiments with a number of different soils showed that their nitrogen-fixing power varied from 0.15 to 14.47 mg. of nitrogen per gram of mannitol consumed.

Mannitol and lactose proved to be the best sugars for maximum fixation in impure cultures, whilst very little fixation was obtained with maltose and sucrose. With pure cultures, mannitol and dextrin gave the best results, and good results were also obtained with sucrose, but not with lactose.

As regards mineral nutrients, di- and tri-calcium phosphates give better results (in impure cultures) than the monocalcium salts.

The period of incubation for impure cultures should be from twenty-one to twenty-eight days. If too prolonged, losses of nitrogen may occur. Calcium carbonate need only be present in very small amounts.

The amount of protein in the cells of *Azotobacter* was found to range from 8.31 to 19.13%, whilst the phosphorus (as P_2O_5) varied from 2.51 to 3.97%. N. H. J. M.

The Products Resulting from the Putrefaction of Fibrin by *Clostridium carnosifetidis*, and the Rauschbrand Bacillus. FRANCIS H. MCCRUDDEN (*J. Biol. Chem.*, 1910, 8, 109—111).—The two micro-organisms mentioned are selected as widely different types of anaerobes. The products of putrefaction of fibrin show distinct differences, Rauschbrand leading, for instance, to the formation of about one-fifteenth of the gases produced by *Clostridium*. The question is to be followed up in the hope that such differences may be of diagnostic value. W. D. H.

Action of Dysentery Bacilli on Nitrites and Nitrates. W. J. LOGIE (*J. Hygiene*, 1910, 10, 143—154).—All the dysentery strains examined with one exception (*B. Neisser*, Ac.) reduced nitrates to nitrites; none which fail to ferment mannitol destroyed nitrites. *B. dysenteriae*, Jürgens, although closely related to *B. dys.*, Flexner, differs from

it in its action on litmus whey, and in failing to destroy nitrite. *B. dys.*, Jürgens, is the only strain found to form indole, and, therefore, to give the cholera-red reaction. The addition of dextrose enables Shiga strains to destroy nitrites. With an abundant supply of oxygen, all the strains fail to destroy nitrites and nitrates, but in media which contain dextrose the inhibitory effect of oxygen is less marked. Under anaërobic conditions, Shiga strains and *B. dys.*, Jürgens, still fail to destroy nitrites.

W. H. D.

The Enzymes in Different Bacteria. EMIL ABDERHÄLDEN, LUDWIG PINCUSOHN, and ADOLF R. WALTHER (*Zeitsch. physiol. Chem.*, 1910, 68, 471—476).—The culture fluids of a paratyphoid-like bacillus and of *Streptococcus pleuro-pneumoniae* have no peptolytic action on various kinds of peptone. *Paratyphus B.* slightly decomposes casein peptone. Various bacilli were grown in different media with and without peptone, and the change in the rotatory power noted. It is hoped that this method, of which a few preliminary examples are given, may be utilised in the differentiation of micro-organisms.

W. D. H.

Amount of Phosphorus in Yeast and in Some Yeast Preparations. EDUARD BUCHNER and HUGO HAEHN (*Biochem. Zeit.*, 1910, 27, 418—426).—Yeast which had been subjected to a pressure of 70 atmospheres was found to contain about two-thirds of the total phosphorus originally present.

Yeast prepared with acetone contains more phosphorus than when acetone and ether are employed. No connexion seems to exist between the fermenting power of yeast and the percentage of phosphorus.

N. J. H. M.

Action of Sodium Selenite on the Production of Carbon Dioxide from Living and Dead Yeast. MARIE KORSKOFF (*Ber. deut. bot. Ges.*, 1910, 28, 334—338).—Whilst a 1% sodium selenite solution completely checks the production of carbon dioxide from zymoin, living yeast produces considerable amounts even in 30% solutions. Small amounts of sodium selenite (0.1—0.5%) even increase the activity of living yeast.

N. H. J. M.

Fermentation of Galactose by Yeast and Yeast Juice. ARTHUR HARDEN and ROLAND V. NORRIS (*Proc. Roy. Soc.*, 1910, B, 82, 643—649).—The results of other investigators showing that some yeasts when cultivated in a medium containing galactose acquire the property of fermenting galactose are confirmed. Yeast trained in this manner yields a juice capable of fermenting galactose.

A fermenting mixture of yeast juice and galactose reacts with phosphate in a manner similar to yeast juice and dextrose. The rate is accelerated; an extra amount of carbon dioxide is evolved, equivalent to the phosphate added, after which the rate again becomes normal. An organic phosphorus compound is produced, which is not precipitated by magnesium citrate mixture. Small amounts of sodium arsenate also accelerate the fermentation of galactose.

N. H. J. M.

Disinfection by Chemical Agencies and Hot Water. HARRIETTE CHICK (*J. Hygiene*, 1910, 10, 237—286).—Further experiments are adduced to show that disinfection is an orderly time process analogous to a chemical reaction between the bacterium and the disinfectant. The destruction of bacteria by water between 45° and 55° is also a consistent time process, and runs parallel to the heat coagulation of proteins; both proceed in accordance with the mass-law and in agreement with the law of Arrhenius in relation to temperature changes. The temperature-coefficient is very high. Disinfection by drying and by sunlight, so far as can be judged by the scanty data at present available, fall into line also. A large number of different micro-organisms were subjected to experiment.

W. D. H.

The Influence of Cell Lipoids on the Autolysis of Wheat Seedlings. MARIE KORSKOFF (*Biochem. Zeitsch.*, 1910, 28, 121—126).—Powdered wheat seedlings were allowed to autolyse, and the amount of proteolysis was estimated; previous extraction of the powder with solvents of lipoids (light petroleum, ether, alcohol, etc.) lessens the amount of autolysis, from which the conclusion is drawn that they have an important influence on the process.

W. D. H.

Rôle of Reduction Processes in the Respiration of Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1910, 28, 319—329).—The reducing power of various seeds, as indicated by methylene-blue, was found to be greatest in peas and least in cereals and oil seeds, whilst wheat and lupins occupy an intermediate position. There is a certain parallelism between the anaerobiose and the reducing power of seeds, since the anaerobiose is highest in leguminous seeds and lowest in cereal and oil seeds (Godlewski and Polzeuizsz, *Abstr.*, 1898, ii, 400; 1901, ii, 618).

Acid salts, such as dihydrogen potassium (or sodium) phosphate, depress the reducing power of pea seeds. Neutral salts and sodium selenite and ammonium vanadate act still more unfavourably. Alkalis, and especially dihasic phosphates, stimulate the reduction process.

N. H. J. M.

Action of Salts on the Respiration of Plants and on the Respiration Enzymes. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1910, 27, 450—473).—All the salts contained in Knop's nutritive solution depress the energy of respiration. An acid reaction is especially injurious, and alkalis also cause a decrease.

Dibasic phosphates considerably increase the production of carbon dioxide in ground living seeds of *Pisum sativum*, *Zea Mays*, and *Lupinus angustifolius*, and in the seeds frozen and killed with acetone. In the case of *Triticum* the energy of respiration was diminished.

Acid phosphates diminish the production of carbon dioxide. Only basic phosphates have a stimulating effect. Phosphates stimulate not only the zymase, but also the oxydases, catalases, and reductases.

As regards the relative amounts, or the relative activity of the reductase and catalase of different seeds, it was found that the activity

of the reductase increased in the following order: *Zea* (0), *Triticum* (1), *Lupinus* (10), and *Pisum* (480), whilst in the case of catalases the order is reversed: *Pisum* (10), *Lupinus* (12), *Triticum* (30), and *Zea* (50).

N. H. J. M.

Importance of Mucilages in the Germination of Seeds. CIRO RAYENNA and M. ZAMORANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 247—253).—Linseed which has been deprived of its mucilago by repeated treatment with water yields fewer seedlings than the untreated seed, and their weight and ash are less than that of normal seedlings. When, however, the sand in which germination is effected is treated with a solution containing sugar and the inorganic constituents found in the mucilage extracted, the weight and ash of the seedlings obtained approximate to those of normal seedlings. This tends to show that the mucilage functions as a reserve food material during germination.

R. V. S.

Lecithin and Lecithides in Germinating Seeds. LUIGI BERNARDINI and G. CHIARULLI (*Bied. Zentr.*, 1910, 39, 594—596; from *Staz. sper. agrar. ital.*, 1909, 42, 97).—Seeds of cereals contain both free and combined lecithin in the proportion of about 1:2. During normal germination both forms of lecithin increase, at about the same rate, until the period of chlorophyll production, after which it decreases. In absence of light, germination is accompanied by a loss of lecithin, chiefly of the combined portion.

N. H. J. M.

Occurrence and Detection of Chlorogenic Acid in Plants. Extraction and Yield of Caffeic Acid from Plants. CHARLES CHAUAUX (*J. Pharm. Chim.*, 1910, [vii], 2, 292—298).—From Gortier's results (*Abstr.*, 1908, i, 186, 345) it appears that caffeic acid in plants results from chlorogenic acid, and the author has therefore devised a quantitative method of extracting caffeic acid from plants, and from the results so obtained he proposes to deduce the quantity of chlorogenic acid present, on the assumption that the latter is equivalent to about half its weight of caffeic acid.

The residue left on distilling the solvent from an alcoholic extract of the finely-ground plant is taken up with warm water and this shaken out twice with ether to remove impurities. The filtered aqueous extract is treated with excess of a solution of basic lead acetate, the precipitate collected, washed, and decomposed with cold dilute sulphuric acid in slight excess, giving a solution of impure chlorogenic acid. This is rendered slightly alkaline, boiled for thirty minutes, and excess of dilute sulphuric acid added. The liberated caffeic acid is extracted with ether, purified by re-crystallisation from boiling water, and weighed. In some cases it requires further treatment for the removal of impurities. A number of colour reactions for the detection of chlorogenic acid are given, and a list of plants in which this acid has been found and estimated as caffeic acid by the process outlined above. The quantity of caffeic acid found varied from 0.6 to 10% for different plants.

T. A. H.

Rôle of Catalase in Plants. ANNA ROSENBERG (*Ber. deut. bot. Ges.*, 1910, 23, 280—288).—Results of experiments with a variety of seeds in which equal weights of the powdered substance were digested for an hour with water and treated with hydrogen peroxide indicated that no direct connexion exists between the anaerobiose and the catalase, since the leguminous seeds acted the least on hydrogen peroxide, whilst the cereal seeds, although little suited to anaerobiose, proved to be very rich in catalase.

Acids, even 0.25% citric acid, are very injurious to catalase, and the acid phosphates of sodium and potassium decrease its activity. Alkali salts, such as sodium carbonate and dibasic phosphates, are favourable, the latter acting most in the case of seeds which only contain small amounts of catalase.

The catalase of lupins is rapidly destroyed by autolysis. Addition of dibasic phosphates protects the catalase from decomposition; the amount, however, gradually diminishes when the temperature is raised.

Whilst the amount of catalase increases during germination, addition of potassium nitrate, magnesium sulphate, potassium dihydrogen phosphate, and calcium nitrate respectively (0.5%) was found to retard the production of catalase.

N. H. J. M.

Alkaloidal Content of Cinchona Leaves. P. VAN LEESEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 210—227).—The researches of Junghuhn, de Vrij (*Abstr.*, 1897, i, 383), Broughton, Howard and Meens have shown on the whole that cinchona leaves contain alkaloids, although they leave some doubt as to the existence of other than amorphous alkaloids in these plant organs. Lotsy's physiological experiments with cinchona leaves (*Ann. Jard. Bot. Buit.*, 1899, 12, 36) indicated that alkaloids are formed in the leaves, whence they are transported to the stem, where the final formation of crystalline alkaloids occurs, and hence are to be regarded as assimilation products. The present paper disproves Lotsy's contention, and shows that the alkaloids, which include quinine and cinchonine, occurring in the leaves are products of metabolism.

The method of estimating the total alkaloids consisted in mixing the ground leaves or bark with slaked lime, sodium hydroxide and ammonia, and extracting with ether, the alkaloids being recovered from the latter in the usual manner, dissolved in *N*/10-acid, and the excess of acid titrated. The results obtained show (1) that exposure of living leaves to light or dark has no effect on their alkaloidal content; (2) that no evidence could be obtained of the transport of alkaloid through the branches to the stem, and (3) that both the mesophyll and veins of the leaves of *C. Ledgeriana* and *C. succirubra* contain the crystalline alkaloids, quinine and cinchonine. These results are on the whole in harmony with those found for *Datura Stramonium* by Feldhaus (*Abstr.*, 1905, ii, 648), and for tea by Du Pasquier (*Inaug. Diss.*, Zurich, 1908), and by Weevers (*Ann. Jard. Bot. Buit.*, 1904, 21, ii, Part 1), with the exception that Weevers found no caffeine in fallen tea leaves, whilst in the present investi-

gation fallen *cinchona* leaves proved to be as rich in alkaloids as the living leaves.

T. A. H.

The Alkaloid of Pituri Obtained from *Duboisia hopwoodii*. A. C. H. ROTHERA (*Bio.-Chem. J.*, 1910, 5, 193—206).—The alkaloid of pituri is nicotine; no evidence was found of the presence of any other alkaloid.

W. D. H.

Action of Ultra-violet Rays on Plants Yielding Coumarin, and on Plants in which the Odour is due to Decomposable Glucosides. JEAN POUGET (*Compt. rend.*, 1910, 151, 566—569. Compare Heckel, this vol., ii, 63).—An odour of coumarin is rapidly developed when the leaves of plants, such as *Melilotus officinalis* or *Asperula odorata*, are exposed for a short time to the light from a quartz-mercury lamp. The leaves become blackened, owing to the death of the protoplasm; the enzymes survive, however, and effect scission of the glucosides. The action of ultra-violet light in this respect is identical with that of cold and anaesthetics (Grignard, *Abstr.*, 1909, ii, 813; Mirande, *ibid.*, ii, 824).

Similar results have been obtained in experiments on the leaves of the cherry laurel and other plants which develop their characteristic odour on exposure to the rays.

W. O. W.

Effect of Poisonous Solutions Containing Alkaloids on Soils and Plants. RICHARD OTTO and W. D. KOOPER (*Landw. Jahrb.*, 1910, 39, 397—407. Compare *ibid.*, 1896, 25, 1007).—Nicotine solutions (0.3%) are very favourable to the growth of *Nicotiana tabacum*, and favourable to *Solanum tuberosum*. In the case of *Nicotiana* the amount of alkaloid was increased, and similar results were obtained with other nitrogenous substances, such as sodium nitrate. The alkaloid had no appreciable effect on the other constituents.

Nicotine is absorbed physically by humus and sandy soils. It partly decomposes in the soil, with production of ammonia, and a part is lost by volatilisation.

N. H. J. M.

Origin and Physiological Function of Pentosans in Plants. II. LEO RAVENNA and O. MONTANARI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 202—207. Compare Ravenna and Coeser, *Abstr.*, 1909, ii, 1046).—The results previously described have been confirmed in most respects by further experiments on the leaves of *Vicia faba minor*. The quantity of pentosans present in the leaves showed a tendency to increase during the day and decrease during the night. A considerable increase occurs when the leaves are supplied with carbohydrate food (dextrose, fructose, sucrose), whilst prevention of the function of the chlorophyll in the leaves and the absence of carbohydrate nutriment cause the amount of pentosans to decrease.

R. V. S.

Chemico-physiological Investigations on the Tubercles of *Vicia faba*. GIOVANNI SANA (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 207—211).—In the fresh plant, the bacteroidal tissue of the tubercles was found to contain 0.965% of nitrogen, the cortical layer

only traces. In the roots, 0.2987% of nitrogen was found, in the stems, 0.1635—0.065%, and in the leaves, 0.707—0.7995%. The non-protein nitrogen in the tubercles amounted to 0.033%. Boiling water extracts various amino-acids from the tubercles; among them *L*-asparagine and glycine were identified.

R. V. S.

Metabolism of Moulds. *Aspergillus fumigatus*. I. CRO RAVENNA and G. PROHINI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 312—316).—From alcoholic extracts of three cultures of *A. fumigatus*, the authors isolated the following three substances respectively: (1) a highly toxic substance, forming colourless, prismatic crystals, m. p. about 300°; (2) mannitol; (3) trehalose.

R. V. S.

Behaviour of Moulds Towards the Stereoisomerides of Unsaturated Dibasic Acids. ARTHUR W. DOX (*J. Biol. Chem.*, 1910, 8, 265—267).—Buchner found that *Penicillium glaucum* and *Aspergillus niger* will grow in media containing ammonium salts of fumaric acid. But they were not able similarly to utilise maleic acid as a source of carbon. The latter is not found in nature; nevertheless, the distinction is surprising, because of the readiness with which the two acids are convertible one into the other. The present experiments, made with a large number of moulds, confirm Buchner's statement. Mesaconic and citraconic acids also resemble maleic acid. Itaconic acid gave a slight growth in a few cases, but no normal colony.

W. D. H.

Amylase of Ungerminated Cereals and Malt. T. CHURAZECZ (*Bied. Zentr.*, 1910, 39, 641—642; from *Zeitsch. Spiritusind.*, 1909, 32).—Malt amylase acts most favourably when 1% potato starch is employed with a temperature between 50° and 55°. The amylase of ungerminated cereals shows the same optimal temperatures for saccharification, but is less active than the amylase of malt. The diastatic power of wheat and rye is greater than that of barley, and still greater than that of oats. The assumption that malt has a special amylase, different from the amylase of resting grain, would therefore seem to be incorrect. It is probable that in cereals the action of the amylase is retarded by some unknown factor (amylum-coagulate).

It is suggested that cereal seeds contain an amylase which does not possess the full enzymatic power, a pro-enzyme which changes to active enzyme during germination.

N. H. J. M.

Composition of Barbados Rain. R. RADCLIFFE HALL and J. R. BOVELL (*Rep. Agric. Work, Barbados; Imp. Dept. Agric. West Indies for 1907-1909*, 3. Compare Brünnich, this vol., ii, 647).—Analyses of fortnightly samples of rain-water from December, 1907, to May, 1909. The average amounts of nitrogen as ammonia and as nitrates in the rain of 1908, and the total amounts per acre, were as follows:

| Rainfall, inches. | Nitrogen per million | | Nitrogen per acre (lb.) | | | Per cent. of Total N. | |
|----------------------|----------------------|-----------------|-------------------------|-----------------|--------|-----------------------|-----------------|
| | as Ammonia. | as Nitrates. | as Ammonia. | as Nitrates. | Total. | as Ammonia. | as Nitrates. |
| 40.28 | 0.032 | 0.334 | 0.295 | 3.498 | 3.793 | 7.8 | 92.2 |

The chlorine in the rain-water amounted to 8.38 per million, corresponding with 76.39 lb. per acre. N. H. J. M.

Analytical Chemistry.

A New Indicator for Alkalimetry and Acidimetry. 6-Sulpho- β -naphthol-1-azo-*m*-hydroxybenzoic Acid. R. MELLER (*Chem. Zeit.*, 1910, 34, 1073—1074).—When 4-amino-3-hydroxybenzoic acid is diazotised and combined with β -naphthol-6-sulphonic acid, a soluble dye is obtained, which may be used as an indicator.

The sodium salt forms dark violet crystals, dissolving readily in water to a violet solution. The acid is also soluble, and forms deep red solutions. Alkalis change the colour to violet, but an excess of alkali causes a change to cherry-red; the indicator is therefore unsuitable for use on test-papers. The indicator is prepared by adding *N*/10-hydrochloric acid to a 1% solution of the sodium salt until the colour is distinctly red. Such a solution is three times as strongly coloured as one of litmus of equal concentration. In *N*/100-solutions of acids or alkalis, the sensitiveness is equal to that of phenolphthalein. C. H. D.

Chart Presentation of Recent Work on Indicators. GEORGE S. WALPOLE (*Bio.-Chem. J.*, 1910, 5, 207—214. Compare this vol., i, 541).—The apparatus previously described is explained more fully, the new method of notation of hydrogen-ion concentration explained, and a diagram is given of how Sørensen's results can be conveniently displayed on a chart. A few examples illustrate how the chart may be used. W. D. H.

Apparatus for Measuring Known Quantities of Liquids. F. HUDIG and M. J. VAN'T KRUYSS (*Chem. Weekblad*, 1910, 7, 179—182).—Six vertical tubes closed by stopcocks at the lower end are sealed at their upper ends into a tube slightly inclined to the horizontal, connected at one end through a stopcock to a water pump, and at the other (lower) through a long vertical tube to the vessel containing the liquid to be measured. A short glass tube sealed into the main tube, and closed with rubber tube and a pinchcock, serves to admit air to the apparatus at will. The liquid is drawn up into the horizontal tube by the water pump, and flows into the vertical stopcock tubes. Definite volumes are marked on these tubes, and can be measured off. The apparatus is specially adapted to the measurement of given volumes of strong acids. A. J. W.

Quantitative Spectral Analysis. WALTHER HEMPEL and ALFRED L. VON KLEMPERER (*Zeitsch. angew. Chem.*, 1910, 23, 1756—1759).—An arrangement is described by means of which certain metals can be quantitatively estimated by spectroscopic observations. The spectroscope is focussed on a oxyhydrogen flame.

supplied with hydrogen and oxygen at constant pressure, and the metals are introduced into the flame by allowing the gases, evolved from an acidified solution of the metal by an electric current of constant strength, to mix with the entering hydrogen. The concentration of the solution under examination is diminished until the characteristic lines of the particular metal just cease to be recognisable in the spectroscope.

From comparative observations under exactly similar circumstances with a standard solution, the concentration of the metal in a solution of unknown strength can be obtained. The method can be applied to the estimation of potassium, lithium, calcium, and thallium, and is recommended for the estimation of the two former in samples of soil. It is shown that the presence of small quantities of other flame-colouring metals is without much influence on the results obtained. Larger quantities lead to an apparent diminution in the quantity of the metal under examination.

H. M. D.

Volumetric Method of Estimating Iodide in Presence of Chloride, Bromide, or Free Iodine. WILLIAM C. BEAY and G. M. J. MACKEY (*J. Amer. Chem. Soc.*, 1910, 32, 1193-1204).—A method of estimating iodides in aqueous solution is described which is based on that suggested by Sammet (*Abstr.*, 1906, ii, 153), and depends on the oxidation of the iodide by potassium permanganate, the removal of the liberated iodine with carbon tetrachloride, and its subsequent titration with standard sodium thiosulphate. Experiments have been made with potassium iodide solutions of known strength, which show that the results obtained by this method are accurate within 0.1%, and are independent of the presence of chlorides, bromides, or copper sulphate. When free iodine is present in the solution to be analysed, it is estimated by direct titration with sodium thiosulphate; the amount of iodine present as iodide is then ascertained by subtracting this quantity from the total iodine.

The estimation may be carried out by titrating the solution directly with potassium permanganate in presence of carbon tetrachloride, since, as the concentration of the potassium iodide is decreased, a larger proportion of the iodine is dissolved by the carbon tetrachloride, until finally the aqueous liquid becomes colourless. It has been found, however, that this method is not entirely satisfactory, since the reduction of the permanganate to the manganous salt is not quite complete, and an error amounting to about 0.4-0.5% of the permanganate solution is thus introduced.

E. G.

Estimation of Fluorine in Aromatic Fluorine Derivatives HANS MEYER and ALFRED HUB (*Monatsh.*, 1910, 31, 933-938).—See this vol., i, 735.

An Ozonometer. STEPHAN JAHN (*Ber.*, 1910, 43, 2319-2321).—The ozonometer consists essentially of a U-tube fitted with stop cocks, one of these being a three-way one, and connecting with a manometer containing paraffin oil. The U-tube is 2 cm. in diameter, and has an internal volume of about 70 c.c.; sealed into it, and running

through its length, is a thin platinum wire, which can be heated by an electric current.

To use the instrument, 150—200 c.c. of the gaseous mixture containing ozone are passed through the U-tube, which is then closed at the inlet. The three-way tap is turned to connect with the manometer, and the liquid in the latter adjusted to a zero mark. The platinum wire is then heated to a dull red heat for five to ten seconds, this time being sufficient to destroy the ozone. When the original temperature has been attained, the manometer is again adjusted to zero, and the increase of pressure determined, from which the percentage of ozone can be calculated. A correction has to be applied for the amount of ozone decomposed while the gas is in contact with the cold platinum wire before the latter is heated. This is determined by a blank experiment.

The method is more exact and quicker than the determination of ozone with potassium iodide.

T. S. P.

The Quantitative Analysis of Some Inorganic Sulphur Acids. ANGELO CASOLARI (*Gazzetta*, 1910, 40, ii, 22—27).—A polythionate containing m atoms of sulphur in the molecule yields $m-1$ molecules of sulphuric acid when treated with hydrogen peroxide and sodium or potassium hydroxide (Abstr., 1908, ii, 222). The solution to be titrated is therefore rendered perfectly neutral, and treated with a pure neutralised solution of hydrogen peroxide and a known volume of $N/10$ -alkali hydroxide. After heating on the water-bath, the excess of alkali is titrated with acid: $\text{Na}_2\text{S}_m\text{O}_6 + (3m-5)\text{H}_2\text{O}_2 + (m-1)\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + (m-1)\text{H}_2\text{SO}_4 + (3m-5)\text{H}_2\text{O}$. The same reaction may be used for thiosulphates: $\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$. Under the same conditions, thiocyanates are decomposed into a sulphate and a cyanate: $\text{KSCN} + 4\text{H}_2\text{O}_2 + 2\text{KOH} = \text{K}_2\text{SO}_4 + \text{KCNO} + 5\text{H}_2\text{O}$. A volume of $N/10$ -sulphuric acid equal to that of the alkali taken is then added, and, after boiling for a few minutes, the acidity of the solution is determined. If ammonium thiocyanate is present, the ammonia must be expelled by boiling with alkali before oxidising.

When a thiosulphate and a thiocyanate are both present in the solution, the sum of the two may be estimated as above, and the thiosulphate estimated separately by means of iodine.

C. H. D.

Detection of Nitrogen in Organic Substances. H. RUSSELL ELMS (*Chem. News*, 1910, 102, 187).—The test described by Castellana (Abstr., 1905, ii, 201) is untrustworthy, owing to the fact that cyanide is formed when powdered magnesium and sodium or potassium carbonate are heated together in a limited supply of air, the nitrogen necessary to the formation of cyanide being obtained from the atmosphere. When, however, the reaction is allowed to proceed rapidly in a copious supply of air, cyanide is not formed. Similar reactions take place when mixtures consisting of magnesium and either calcium carbonate, barium carbonate, or strontium carbonate are heated in contact with a small amount of air; in these cases, cyanide, cyanamide, nitride, and carbide are formed.

W. P. S.

Estimation of Ammonia Nitrogen in Water in Presence of Hydrogen Sulphide. EDWARD BARTOW and B. H. HARRISON (*J. Amer. Chem. Soc.*, 1910, 32, 1256—1259).—The presence of hydrogen sulphide in a water interferes with the Nessler test. When a large amount of ammonia is present, the hydrogen sulphide may be removed by precipitation with a salt of zinc or lead, and the ammonia can then be estimated directly by the Nessler reagent. If, however, the quantity of ammonia is small, and it is desirable to distil and test the distillates, the results obtained are inaccurate. It has been found that accurate results can be obtained by the following method. To 500 c.c. of the water, a measured quantity of *N*-sulphuric acid is added, and 100 c.c. are distilled; by this means the hydrogen sulphide is completely removed. A volume of *N*-sodium hydroxide equal to that of the sulphuric acid used is now added, the water is again distilled until 200 c.c. have collected, and the Nessler test is applied to the distillate. E. G.

Estimation of Small Quantities of Nitrogen by Pelouze's Reaction. A. T. DAVENPORT (*J. Amer. Chem. Soc.*, 1910, 32, 1237—1241).—A method is described for estimating small quantities of nitrogen occurring in the form of nitrates by Pelouze's reaction, which consists in the oxidation of ferrous chloride in presence of hydrochloric acid. A diagram of the apparatus is given.

The most important features of this method are the measurement of the volume of gas over sodium hydroxide solution in a jacketed burette, graduated to 1/20 c.c., as in the Schultze-Tiemann method, and the correction of the volume by comparison with a standard volume contained in another burette under exactly the same conditions. The process is simple and easily manipulated, permits of an estimation being carried out in ten minutes, and gives accurate results. E. G.

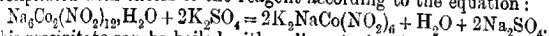
Easy Detection of Arsenic; Rapid Separation of Arsenic and Some Other Metals from Liquids. C. E. CARLSON (*Zeitsch. physiol. Chem.*, 1910, 68, 243—262).—On adding hydrogen sulphide to an acid solution of arsenious acid, or thioacetic acid to a solution of arsenic acid, arsenious sulphide is precipitated, but if the amount is only a fraction of a mg., the separation takes a long time. If, however, ether is added, or preferably a mixture of ether and chloroform, and the whole well shaken, the ethereal layer contains all the arsenious sulphide in suspension or in pseudo-solution. Addition of alcohol promotes the separation. On being evaporated on the water-bath, arsenious sulphide is left, which may then be further identified by the mirror test. When testing urine (or other organic liquid), this is evaporated to dryness and the residue is distilled with hydrochloric acid and some ferric chloride; the distillate is diluted with solution of hydrogen sulphide and shaken with ether. The quantitative process is, briefly, as follows: The ethereal residue is heated with 1 c.c. of 30% sulphuric acid and 2 c.c. of 5% potassium permanganate for ten to fifteen minutes. The arsenic acid formed is reduced to the arsenious state by heating for half an hour at 50—70° with addition of 10 c.c. of strong solution of sulphur dioxide, and the

solution is finally evaporated nearly to dryness. Another 5 c.c. of sulphur dioxide are added, and the evaporation is repeated. The residue is now dissolved in 15 c.c. of water, 2 grams of sodium hydrogen carbonate are added, and the arsenic is titrated with *N*/100-iodine with starch as indicator.

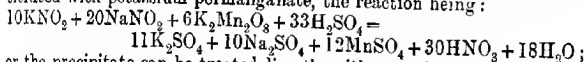
Other sulphides, such as those of lead and mercury, are also taken up readily by ether.

L. DE K.

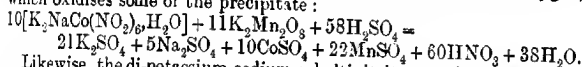
Estimation of Potassium by the Cobaltinitrite Method. L. T. BOWSER (*J. Ind. and Eng. Chem.*, 1909, 1, 791—798).—A detailed account of the methods employed, and the results obtained by previous workers, those of Drushel and of Adie and Wood being fully discussed, and stated to be unsatisfactory in several ways when repeated by the author, who suggests the following modifications. The potash is brought into solution, any excess of acid driven off, and the residue boiled with sodium carbonate to remove any interfering metals, the filtrate concentrated, acidified with acetic acid, and the potassium precipitated with excess of the reagent according to the equation:



This precipitate can be boiled with sodium hydroxide, the precipitated cobalt hydroxide, $\text{Co}(\text{OH})_2$, separated, and the filtrate and washings titrated with potassium permanganate, the reaction being:



or the precipitate can be treated directly with potassium permanganate, when a more complicated reaction occurs, owing to trivalent cobalt being reduced to bivalent, and thereby releasing one atom of oxygen, which oxidises some of the precipitate:



Likewise, the di-potassium-sodium-cobaltinitrite may be collected on asbestos, oxidised by hot standard potassium permanganate, which is decolorised by an excess of standard oxalic acid, and then titrated back with permanganate.

The influences exerted on the reaction by (1) varying the concentrations of the solutions; (2) the presence of other salts, and (3) the acid with which the potassium is combined are also investigated, and the results tabulated.

F. M. G. M.

Rapid Estimation of Copper, Silver, Cadmium, and Bismuth by means of the Mercury Cathode and Stationary Anode. RAYMOND C. BENNER (*J. Amer. Chem. Soc.*, 1910, 32, 1231—1237).—Stoddard (Abstr., 1909, ii, 347) has described a method of electroanalysis by means of a mercury cathode and a stationary platinum gauze anode, in which the evolution of the gas by the current causes sufficient agitation of the liquid to enable the metals to be deposited in an adherent form. This method has now been applied to the estimation of copper, silver, cadmium, and bismuth. The apparatus is as simple as any other form of electrolytic apparatus employed for the purpose, the metal is deposited nearly as rapidly as by the rotating anode and mercury cathode, and the results are as accurate as those obtained by other methods in which mercury is used as the cathode.

The precipitation is complete in twenty minutes with copper, ten minutes with silver and cadmium, and twenty-five minutes with bismuth.

E. G.

Volumetric Estimation of Mercury by means of Ammonia. G. BRESSANIN (*Boll. chim. farm.*, 1910, 49, 589—591 *).—Archetti's method, based on the estimation of the acid liberated according to the equation $\text{HgCl}_2 + \text{NH}_3 = \text{NH}_2\text{HgCl} + \text{HCl}$, only gives quantitative results when four times the molecular quantity of ammonia is taken for the reaction, the excess being afterwards estimated by titration with litmus.

R. V. S.

Estimation of Indium with the Use of a Mercury Cathode. LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, 32, 1248—1250).—It has been found that the indium in a solution of indium sulphate containing a little free acid can be satisfactorily estimated electrolytically with the use of a rotating mercury cathode. When 10 c.c. of the solution containing about 0.10 gram of metal were used, with a current of 2—4 amperes, an *E.M.F.* of 6.5—7.5 volts, and an anode rotating 750 times per minute, the precipitation was complete in fifteen minutes. Estimations were also made by using a platinum cathode and a rotating platinum spiral anode; in presence of 0.1 c.c. of concentrated sulphuric acid and a few drops of gelatin, an adherent deposit of indium was obtained in twenty-five minutes. A potassium cyanide electrolyte and one containing Rochelle salt also proved satisfactory.

E. G.

Volumetric Method for the Estimation of Manganese. FLOYD J. METZGER and ROBERT F. McCRACKAN (*J. Amer. Chem. Soc.*, 1910, 32, 1250—1251).—Metzger and Heidelberger (this vol., ii, 658) have stated that when a solution of manganese in sulphuric acid is treated with sodium bismuthate, it is oxidised to the quadrivalent state. A method has now been devised for estimating manganese by means of this reaction.

Fifty c.c. of a standard manganese solution are treated with 10—15 c.c. of concentrated sulphuric acid, 1—2 grams of finely-powdered sodium bismuthate are added to the cooled liquid, and the mixture is heated in a water-bath until the basic bismuth compound subsides in a granular form. The flask is cooled, a known excess of ferrous sulphate solution is added, the liquid is diluted to about 200 c.c., and titrated back with standard potassium permanganate. The value of the permanganate in terms of iron multiplied by 0.4918 gives the value in terms of manganese.

The method is rapid, and the end-point is sharp and distinct. It is being applied to the analysis of *spiegel* and manganese ores. E. G.

Estimation of Manganese in Potable Water. J. RODENBERG (*Chem. Weekblad*, 1910, 7, 877—879).—As the tint of the solution of permanganate obtained in the estimation of manganese in potable water by the persulphate method usually differs from that of the colorimetric standard made from potassium permanganate, the author employs as standard one or more c.c. of a solution of manganese

* and *Ann. Chim. anal.*, 1910, 15, 413—419.

ammonium sulphate containing 0.0025 gram Mn_2O_3 per litre, this solution being oxidised with persulphate in the same way as the sample under investigation. This difference of tint being due to chlorides in the sample, they must be eliminated. The author's procedure is as follows: 50 c.c. of the sample are boiled for several minutes with 5 c.c. of 50% nitric acid, a slight excess of silver nitrate solution added, and then 10 c.c. of a 10% solution of ammonium persulphate. The solution is brought to the boiling point, cooled, and compared with the standard tint. The method will show the presence of 0.025 mg. of Mn_2O_3 .

A. J. W.

Detection of Small Quantities of Manganese in Foode. DUMITRESCU and E. NICOLAU (*Ann. Falsif.*, 1910, 3, 370—372).—The material is incinerated, the ash is treated with nitric acid, evaporated to dryness, the residue is dissolved in water, and the solution is filtered. A portion of the filtrate is then mixed with an equal volume of a 40% ammonium persulphate solution, 1 drop of a 2% cobalt nitrate solution is added, and the mixture is heated to boiling. Should manganese be present, a pink coloration develops, due to the formation of permanganate. The authors have detected the presence of manganese in such substances as flesh, brain, hilec, peas, beans, lentils, cereals, plums, eggs, milk, wine, etc., by means of this test.

W. P. S.

Error in Permanganate Titrations. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1910, 32, 1204—1207).—It has been shown by Bray and MacKay (this vol, ii, 996) that when an iodide is titrated directly with potassium permanganate, the latter is not completely reduced to the manganous state and an error results, amounting to about 0.10 c.c. of a 0.12N-permanganate solution. It is evident therefore that the reduction of the permanganate takes place in stages, and it is probable that a similar error may occur in other cases of titration with this salt. Škrabal (Abstr., 1908, ii, 17) has shown that the reduction from the manganic to the manganous state by oxalic acid is a slow reaction, and that a stable complex is formed between the manganic salt and the oxalic acid.

Experiments have therefore been made to ascertain the conditions in which the error due to incomplete reduction of permanganate is appreciable in oxalic acid titrations, and it has been found that the error varies from 0.01 to 0.14 c.c. of a 0.12N-permanganate solution, and is negligible if the acid is present in only small amount and the final temperature is 70—80°.

An investigation is being carried out with the object of determining whether there is an appreciable error in the titration of ferrous sulphate solutions with permanganate.

E. G.

The Determination of Iron and Aluminium in Inorganic Plant Constituents. R. F. HARE (*J. Ind. and Eng. Chem.*, 1910, 2, 27—28).—The estimation of iron and aluminium in the presence of manganese, calcium, magnesium, and phosphoric acid is a difficult one, and no satisfactory process has been suggested previously.

A solution of, and representing one gram of, the ash is treated with more than sufficient pure ferric chloride to combine with all the phosphoric acid; sodium carbonate is added until a permanent precipitate is just formed, which is then redissolved with 1 c.c. of 80% acetic acid, and the solution boiled for three or four minutes and rapidly filtered; the precipitate is dissolved in hydrochloric acid, and the iron and aluminium reprecipitated with ammonium hydroxide, dried, ignited, and weighed; this weight, minus the phosphoric acid and ferric oxide (found by other methods) and the ferric oxide added, will give the weight of aluminium oxide in the ash. A great deal depends on the proper adjustment of the amounts of sodium carbonate and of acetic acid added, an excess of either causing serious error. The addition of ferric chloride gives a more easily filtered and washed precipitate, and ensures complete precipitation of phosphoric acid.

The iron is determined in a fresh solution of the ash by the Zimmermann-Reinhardt method, the ferric iron being instantly reduced with stannous chloride, and titrated with potassium permanganate in the presence of hydrochloric acid after the addition of a "titrating solution" of manganese sulphate, phosphoric and sulphuric acids.

This method is claimed to be more accurate and rapid than when zinc is employed for the reduction of the ferric salt. F. M. G. M.

Estimation of Ferrous Oxide in Silicates. MAX DITTRICH and A. LEONHARD (*Ber. Vers. Oberrheinisch. Geol. Ver.*, 1910, ii, 92—93).—The process usually employed is that recommended by Pebel-Döller, consisting in heating the silicate with a mixture of sulphuric and hydrofluoric acid in an atmosphere of carbon dioxide. The solution is then titrated with permanganate as usual.

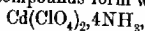
The authors, however, state that if the silicate contains manganese also, the titration proceeds in an irregular manner, and the results become untrustworthy. This may be prevented by adding to the acid mixture 1—2 grams of potassium sulphate; the titration will then proceed normally. L. DE K.

Ammonium Perchlorate as a Reagent. Metalamines Perchlorates. ROBERTO SALVADORI (*Gazzetta*, 1910, 40, ii, 19—21).—Perchlorates of the metallic amines are obtained by adding a 20% solution of ammonium perchlorate in ammonia, D 0.90, to ammoniacal solutions of metallic salts. Precipitation is complete in the case of cobalt, nickel, manganese, and cadmium, even in dilute solutions. Zinc is incompletely precipitated, and copper only slowly from very concentrated solutions. The mercury precipitate is soluble in an excess of the reagent. The method may be used for the separation of cadmium from the sulphides of the second group. The sulphides are dissolved in nitric acid, excess of ammonia is added, and the bismuth is removed by filtration. The ammoniacal solution of ammonium perchlorate is added to the filtrate, and the cadmium is immediately precipitated, carrying with it a small quantity of copper.

The reagent may also be used to separate a cobalt salt from a cobalt-amine salt. In presence of an excess of ammonium perchlorate, and out of contact with air, cobalt is completely precipitated as the compound

$\text{Co}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$, the cobaltammine remaining in solution (compare this vol., ii, 959).

The cadmium and zinc compounds form white crystals,



and $\text{Zn}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$ stable at 100° , melting at about 220° , and decomposing rapidly at 250° . They explode by percussion or if heated rapidly.

C. H. D.

Detection of Small Quantities of Nickel. ALBERTO BIANCHI and ETTORE DI NOLA (*Boll. chim. farm.*, 1910, 49, 517—520).—Nickel-plating may be recognised without damage to the object by moistening it with a drop of acid, which is then absorbed by blotting paper or allowed to fall on to a porcelain surface, rendered alkaline with ammonia, acidified with acetic acid, and tested with dimethylglyoxime. In the presence of acetic acid there is no possibility that the red coloration will be masked by other coloured substances (cupric hydroxide, ferric hydroxide).

R. V. S.

Estimation of Tin in Presence of Antimony. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1910, [iv], 7, 890—894).—The process depends on the fact that whilst ferric chloride is reduced quantitatively by stannous chloride, it is unaffected by antimonous chloride.

In the case of a simple mixture of the two chlorides, the solution is titrated with a standard ferric chloride solution in presence of hydrochloric acid, the formation of a permanent greenish-yellow coloration being taken as the end-point. Where both substances must be estimated, they are converted into their sulphides in the usual manner, and the mixture of sulphides treated with hydrochloric acid and potassium chlorate. To this solution aluminium is added, and when the reduction is completed, the antimony is filtered off and the filtrate and washings diluted to a known volume with diluted hydrochloric acid (50%) and titrated with a ferric chloride solution, which has been standardised against a solution of stannous chloride containing the equivalent of 1% of tin. The precipitated antimony is dissolved by means of hydrochloric acid and iodine solution, and estimated as the sulphide. 0.1 Gram of tin in presence of 1.1 gram of antimony can be estimated accurately by this method.

T. A. H.

Analysis of Tin-Antimony Alloys. LEROY W. MCCAY (*J. Amer. Chem. Soc.*, 1910, 32, 1241—1248).—It has been shown in an earlier paper (*Abstr.*, 1909, ii, 351) that the separation of tin and antimony can be effected by taking advantage of the fact that when a dilute solution of hydrofluoric acid, containing tin in the stannic condition and antimony in the antimonious state, is treated with hydrogen sulphide, only the antimony is precipitated.

The following method is recommended for the analysis of alloys of tin and antimony. From 0.5 to 1 gram of the alloy in the form of filings or fine borings is heated rapidly with concentrated sulphuric acid in a quartz or porcelain dish until fumes of sulphuric anhydride begin to escape, and the heating is then continued for half an hour. If the liquid is now clear and the residue, consisting of lead sulphate, is

quite white, the dish is cooled and its contents are transferred to a 250 c.c. platinum dish containing 5 c.c. of hydrofluoric acid (18%) and 20 c.c. of water. The solution is heated until it boils, and is then diluted to 150 c.c., and 50 c.c. of 95% alcohol are added. When the lead sulphate has subsided, it is collected, washed with water containing one-fourth of its volume of alcohol and a little sulphuric acid, and is dried, ignited, and weighed. The filtrate is collected in a large platinum dish, diluted to about 450 c.c., and treated with a rapid current of hydrogen sulphide for an hour. The precipitate is collected, washed with a saturated solution of hydrogen sulphide containing acetic acid, and afterwards digested repeatedly with colourless sodium sulphide solution. The cupric sulphide, which is left after this treatment, is dissolved in nitric acid, and the copper estimated electrolytically. The sodium sulphide solution is acidified with sulphuric acid, and the antimony precipitate is converted into the black anhydrous sulphide. The tin in the filtrate from the copper and antimony sulphides may be estimated by evaporating the liquid and subsequently heating it until sulphuric anhydride fumes are evolved, and precipitating the tin as stannic acid by pouring the sulphuric acid solution into an excess of water. E. G.

Separation of Bismuth from Alloys containing also Lead and Tin. CHARLES E. SWETT (*J. Ind. and Eng. Chem.*, 1910, 2, 28).—The following expedient is suggested as a means of overcoming the difficulties usually experienced in this estimation. The nitric acid filtrate from the stannic oxide is treated with a moderate excess of potassium or sodium hydroxide, which precipitates bismuth and cadmium, if present, and redissolves the lead hydroxide. The hydroxides are collected, washed, and redissolved in hydrochloric acid, the bismuth being then separated as oxychloride by pouring into a large quantity of water. F. M. G. M.

Rapid Methods for the Analysis of Water. ARISTIDE DAMÉ (*Chem. Zeit.*, 1910, 34, 1057—1058).—In order to ascertain whether a water is suitable for drinking, the author recommends that the following estimations be made: The calcium and magnesium present may be estimated volumetrically, the former by the titration of its oxalate, after this has been precipitated and separated in the usual way, and the latter by precipitating it as ammonium magnesium phosphate and titrating this salt with a uranium solution. Sulphates are titrated with barium chloride solution, and the total carbon dioxide is titrated with barium hydroxide-sucrose solution, allowance being made for the alkalinity of the water. Nitrites are estimated colorimetrically by means of the indole reaction, and the proportion of organic matters is estimated by heating the water with permanganate solution in the presence of sodium carbonate. The organic matters may also be estimated by titration according to Deniges' cyanide-silver nitrate method. Should further information be required as to the quality of the water, the ammonia, chlorides, nitrates, etc., may be estimated, the usual methods being employed for the purpose.

In addition, tests may be applied for the detection of *Eacterium coli*. W. P. S.

Acid Content of Moor Water. KURD ENDELL (*J. pr. Chem.*, 1910, [ii], 82, 414—422).—The acidity of moor water has been determined by direct titration with *N*/100-potassium hydroxide. The method of adding standard barium hydroxide and titrating the excess does not give trustworthy results, the titre decreasing with time, probably owing to the action of the alkali on humus substances present as sols. Before titration, it is necessary to dialyse the water in order to get rid of humus substances. The moor water of the red and of the black moors of the Rhone are 0.007 normal. The water of the Paulsborner moor is 0.0063 normal, the acidity being due entirely to carbonic acid.
C. S.

Estimation of Butyl and Amyl Alcohols in Alcoholic Liquids. A. LASSERRE (*Ann. Chim. anal.*, 1910, 15, 338—341).—Instead of estimating the total quantity of higher alcohols in alcoholic liquids as is done in the Allen-Marquardt process, the method described by the author limits the estimation to that of butyl and amyl alcohols; propyl alcohol is eliminated by treating the alcoholic liquid with carbon disulphide, which extracts the butyl and amyl alcohols. After oxidation, the butyric and valeric acids are extracted from the solution by means of benzene, and their quantity estimated by titration. The details of the process are as follows: 100 c.c. of the alcoholic liquid, 70 c.c. of carbon disulphide, and 450 c.c. of saturated sodium chloride solution are placed in a separating funnel, and after the addition of a quantity of water sufficient to redissolve the precipitated sodium chloride, the mixture is shaken for five minutes. The carbon disulphide is then separated, and the extraction is twice repeated, the united carbon disulphide extracts being next shaken three successive times with moderately concentrated sulphuric acid. The sulphuric acid extract is now heated to 60° in order to remove any traces of carbon disulphide, then diluted with 20 c.c. of hot water, and 5 grams of potassium dichromate and 1 c.c. of concentrated sulphuric acid are added. The whole mixture is then heated in a closed flask for one hour at 50°, cooled, and diluted to a volume of 100 c.c. Twenty-five c.c. of this solution are shaken for three minutes with 30 c.c. of benzene, the latter is separated, filtered, mixed with an equal volume of alcohol, and the solution is titrated with *N*/20-alcoholic potassium hydroxide solution, using phenolphthalein as indicator. The quantity of alkali used in the titration may be calculated into amyl alcohol, but the result obtained must be multiplied by 2.082, this being the ratio of the total amount of the acids present to that portion which is obtained by one extraction with benzene. A method has been described previously (*Abstr.*, 1907, ii, 991) for the separate estimation of butyric and valeric acids.
W. P. S.

Physico-chemical Estimation of the Ash of Wine. HENRI PELLET (*Ann. Chim. anal.*, 1910, 15, 385).—It is pointed out that the conductivity process described by Dutoit and Dubouix (this vol., ii, 552) has already been applied to the estimation of mineral matters in various substances; twenty years ago, Reichert employed the method for the estimation of ash in sugars, etc., but the results

obtained were unsatisfactory. More recently, Main, in a paper submitted to the Seventh International Congress of Applied Chemistry, London, 1909, gave the details of procedure necessary for the correct estimation of ash in sugar syrups by this process. W. P. S.

Polarimetric Estimation of Sucrose in Presence of Reducing Sugars. P. LEMELAND (*J. Pharm. Chim.*, 1910, [vii], 2, 298—302*.)—The method is based on the observation made by Cross, Bevan, and Smith (*Trans.*, 1898, 73, 463) that hydrogen peroxide destroys the optical activity of reducing sugars, forming products eventually identified by Morrell and Crofts as osones (*ibid.*, 1899, 75, 786). The author finds that lactose and dextrose are attacked by hydrogen peroxide in presence of manganese dioxide, forming optically inactive products, whilst sucrose remains unaffected. If, therefore, the optical activity of a solution containing one of these sugars and sucrose is known, the amount of sucrose can be estimated by a determination of the optical activity after the effect of the reducing sugar has been eliminated. Where a small quantity of sucrose occurs with much dextrose, the latter may be almost completely separated by treatment with alcohol of 91° (Lindet, *Abstr.*, 1894, ii, 64), and the part soluble in alcohol may then be recovered and treated as described above.

This method is not applicable where sucrose occurs with maltose. Details of the method of working are given in the original.

T. A. H.

Detection of Inositol as a means of Identifying Wine Vinegar. P. FLEURY (*J. Pharm. Chim.*, 1910, [vii], 2, 264—266).—A number of samples of genuine wine vinegar examined by the author all contained distinct quantities of inositol; the detection of inositol is, therefore, considered to be of use in determining the genuineness of a sample of wine vinegar. If inositol is not present, the sample is probably prepared from alcohol and not from wine. The method described previously by Meillere and Fleury (this vol., ii, 553) may be employed for detecting the inositol. W. P. S.

Estimation of Formaldehyde. WALTER BRÄUTIGAM (*Pharm. Zentr.-h.*, 1910, 51, 915—916).—The process described depends on the decomposition of formaldehyde by calcium hypochlorite; calcium carbonate is formed, and its quantity is a measure of the amount of formaldehyde present. The reaction proceeds according to the equations: $\text{CH}_2\text{O} + \text{CaOCl}_2 = \text{HCO}_2\text{H} + \text{CaCl}_2$; $\text{HCO}_2\text{H} + \text{CaOCl}_2 = \text{CO}_2 + \text{H}_2\text{O} + \text{CaCl}_2$; and $2\text{CaOCl}_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{CaCl}_2 + 2\text{HClO}$. One molecule of formaldehyde therefore yields one molecule of calcium carbonate. In carrying out the estimation, a definite volume of the formaldehyde solution is mixed in a flask with an excess of freshly prepared calcium hypochlorite solution, and the mixture is placed aside for some hours at the ordinary temperature. The clear supernatant liquid is then passed through a weighed filter, and the filtrate is heated almost to boiling in order to ascertain whether all the

* and *Ann. Chim. anal.*, 1910, 15, 415—419.

formaldehyde has been decomposed; should such be the case, the solution remains clear, but if a further quantity of calcium carbonate forms it must be collected on the filter together with the main bulk of the precipitate. The precipitate and filter are washed until free from chlorides, dried at 100° , and weighed.

W. P. S.

Estimation of Formic Acid in the Presence of Acetic Acid. II. DELEHAYE (*Ann. Falsif.*, 1910, 3, 386—388).—The method proposed depends on the reduction of mercuric sulphate to insoluble mercurous sulphate. A quantity of the solution under examination, containing not more than 0.2 gram of formic acid, is mixed with 50 c.c. of mercuric sulphate solution (prepared as described below) and boiled under a reflux apparatus for forty-five minutes. The mixture is then cooled rapidly, the liquid is decanted through a weighed filter, and the volume of the filtrate is measured; the precipitate is then rinsed on to the filter with the aid of a saturated mercurous sulphate solution, washed with 50% alcohol, dried at 110° , and weighed. To the weight found is added a quantity in the proportion of 0.20 gram for every 100 c.c. of the filtrate; the weight thus corrected is then multiplied by 0.0927 to obtain the amount of the formic acid. The mercuric sulphate solution employed is prepared by mixing 10 grams of mercuric oxide with 20 c.c. of hot water, adding sulphuric acid until the oxide has dissolved, and diluting the mixture to a volume of 250 c.c. The filtrate obtained in the estimation should measure not less than 100 c.c., and the filtration must be carried out immediately the mixture has been cooled in order to prevent contamination of the mercurous sulphate with mercuric sulphate, which is liable to crystallise out subsequently.

W. P. S.

The Separation and Estimation of Aspartic and Glutamic Acids. THOMAS B. OSBORNE and LEONARD M. LIDDLE (*Amer. J. Physiol.*, 1910, 23, 420—425).—Aspartic and glutamic acids react acid to litmus, but their acid sodium salts do not. By Fischer's method of protein analysis, glutamic hydrochloride is usually contaminated with leucine hydrochloride, and the two cannot be separated by direct crystallisation. When, however, the solution is made neutral to litmus, leucine crystallises out readily, and from the mother liquor it is possible to separate out a further large amount of glutamic hydrochloride. It was found possible to effect a fairly satisfactory separation of leucine and aspartic acid by taking out a small fraction of the esters after most of the leucine had distilled over and before the aspartic ester begins to distil freely, and then treating this separately by a method described with detail in the text.

W. D. H.

Methods for the Detection and Volumetric and Gravimetric Estimation of Salicylic Acid in Wines, and its Detection in Cases of Poisoning. GIUSEPPE CATTINI (*Boll. chim. farm.*, 1910, 49, 641—649).—For the detection of salicylic acid in wine, urine, and other coloured organic products, acidification and subsequent extraction with toluene are recommended, this solvent being preferable to ether because it does not remove colouring matter from the aqueous liquid.

Various methods which have been proposed for the estimation of salicylic acid are shown to be inaccurate.

R. V. S.

Estimation of Fat in Flesh. G. DIESSSELHORST (*Pflüger's Archiv*, 1910, 134, 496—500).—The fat extracted from flesh or tissue by Dormeyer's process (digestion with pepsin, extraction of the digest with ether, and weighing the ethereal extract) is very impure, and, consequently, the results yielded by the method are untrustworthy. It is shown that if the dry powder is first extracted with ether in a mill, as described by Lehmann and Völtz (*Abstr.*, 1903, ii, 702), the fat obtained has the chemical and physical properties of beef fat. When the extracted residue of flesh is subjected to further treatment by Dormeyer's process, an additional small quantity of "fat" is obtained, which is largely contaminated with substances other than beef fat.

W. P. S.

Estimation of Coconut Oil in Admixture with Butter Fat. NOEL C. CASSAL and B. HENRY GERRANS (*Chem. News*, 1910, 102, 190—191).—In the process described, the fatty acids obtained from the fat are subjected to a somewhat prolonged distillation with steam at a high temperature in order to increase the difference between the titration number of the insoluble volatile fatty acids from coconut oil and the titration number of the insoluble volatile fatty acids from butter fat. The process is as follows: 3 grams of the fat are saponified by heating with 10 c.c. of alcohol and 2 c.c. of 50% sodium hydroxide solution; after the alcohol has been removed by evaporation, the residual soap is dissolved in 50 c.c. of boiling water, 10 c.c. of concentrated hydrochloric acid are added, and then 50 grams of anhydrous calcium chloride. The flask is now connected with a condenser and heated by means of a calcium chloride bath, b. p. 141—116°, and when the contents of the flask begin to boil, steam is admitted and the distillation is continued until 500 c.c. of distillate have been collected. The distillate is filtered as it distils over, and the filtrate is collected in a 500 c.c. flask. At the end of the distillation, the condenser tube and the fatty acids on the filter are washed with cold water to remove hydrochloric acid and soluble fatty acids, the insoluble fatty acids are then dissolved from the condenser tube and the filter by means of hot alcohol, and the solution is titrated with *N*/10-barium hydroxide solution. In the case of coconut oil, the insoluble volatile fatty acids require 66 c.c. of *N*/10-alkali for neutralisation, whilst those from butter fat require 16 c.c.

W. P. S.

Alkylamines as Products of the Kjeldahl Digestion. C. G. ERDMANN (*J. Biol. Chem.*, 8, 41—55).—Compounds containing the groups =NMe , =NHMe , or NMe_2 can yield mono-, di-, or tri-methylamine on digestion with sulphuric acid and a catalyst. The separation of organic base from ammonia in the Kjeldahl distillate is effected by adding to the neutralised solution 5—10 c.c. of an alkaline mixture containing 20% of sodium hydroxide and 30% of sodium carbonate, and 0.1 gram of yellow mercuric oxide for every c.c. of *N*/10-base present. After shaking for one hour in the dark, and keeping till the mercury

has settled, an aliquot part of the supernatant liquid is distilled. The ammonia is retained by the mercuric oxide, and the organic base which distils is titrated. The ammonia is then estimated by difference.

The author suggests that the method can be used as a general qualitative method for determining in nitrogeous substances the presence of alkylamine groups, and can probably also be used for approximately quantitative determinations as well. G. S. W.

Vortmann's Nitroprusside Reaction for Hydrogen Cyanide. H. J. VAN GIFFEN (*Pharm. Weekblad*, 1910, 47, 1043).—A modification of Vortmann's process for the detection of hydrogen cyanide. Although not quite so delicate as the original method, it has the advantage of not being interfered with by the presence of alcohol.

To a portion of the distillate are added a few pieces of sodium nitrite and then 2 or 3 drops of officinal ferric chloride solution. To the brownish-yellow liquid is then added dilute sulphuric acid drop by drop, when effervescence takes place and the liquid turns bright yellow. After heating to boiling, the iron is precipitated by adding excess of ammonia, and the filtrate is evaporated to dryness on the water-bath. The residue is dissolved in a little water, and the solution cooled in ice. On adding a drop of dilute ammonium sulphide, a violet colour is formed, which, according to the amount of cyanide present, more or less rapidly passes into blue, green, and yellow. L. DE K.

Estimation of Nitrogen Existing as Cyanamide and as Dicyanodiamide in Calcium Cyanamide. ALBERT STUTZER and J. SÖLLI (*Zeitsch. angew. Chem.*, 1910, 23, 1873—1874).—An extract of calcium cyanamide is first prepared by shaking the substance (10 grams) with 400—450 c.c. of water for two and a-half hours in a rotary apparatus. The flask is then filled to the mark (500 c.c.) and the contents filtered.

The nitrogen in the form of cyanamide is estimated in 25 c.c. (= 0.5 gram of substance) by adding 10 c.c. of silver acetate solution (prepared by adding 400 c.c. of 10% ammonia to 100 grams of silver acetate and diluting to 1 litre). The precipitate is collected on a nitrogen-free filter, and after all the solution has run through and the beaker below the filter has been changed, is washed with water, and the nitrogen determined by the Kjeldahl method.

The nitrogen as dicyanodiamide is estimated in the undiluted filtrate from silver cyanamide (25 c.c. = 0.357 gram of original substance) by adding 10 c.c. of 10% potassium hydroxide solution, and estimating the nitrogen in the precipitated silver dicyanodiamide.

In directly estimating the dicyanodiamide, an alcoholic extract is made by shaking the substance (10 grams) for an hour with 250 c.c. of 94% alcohol. A portion of the filtered extract (100 c.c.) is evaporated to dryness, dissolved in hot water, treated with 10 c.c. of the silver acetate solution, filtered, and the precipitate washed. The filtrate is then mixed with 10 c.c. of 10% potassium hydroxide, at once filtered, and then estimated by Kjeldahl's method.

N. H. J. M.

Calcium Cyanamide; its Analysis and the Changes in Composition it Undergoes when Exposed to the Atmosphere. CH. BRIOUX (*Ann. Chim. anal.*, 1910, 15, 341-346).—Calcium cyanamide gradually undergoes decomposition when exposed to moist air, the calcium being converted into calcium hydroxide and carbonate, and cyanamide is liberated; the latter polymerises to form a double molecule, dicyanodiamide. All these changes proceed more rapidly when the air contains carbon dioxide and is saturated with moisture; under these conditions, as much as 80% of the soluble nitrogenous compounds present in calcium cyanamide may be converted into dicyanodiamide in the course of a few months. As dicyanodiamide has toxic properties and is injurious to vegetation, it is of some importance to know to what extent the decomposition has proceeded in any sample of calcium cyanamide which has been stored in sacks or bags. This may be ascertained by estimating the cyanamide and dicyanodiamide present in a solution of the calcium cyanamide, and the process recommended for the purpose depends on the fact that cyanamide yields a precipitate with silver nitrate which is insoluble in excess of ammonia, whilst the analogous precipitate obtained in the case of dicyanodiamide is soluble in ammonia; further, both substances are precipitated by silver nitrate in the presence of potassium hydroxide. One gram of the calcium cyanamide is shaken with 250 c.c. of water for three hours, and the solution is then filtered; 100 c.c. of the filtrate are now treated with 20 c.c. of 5% silver nitrate solution, and an excess of ammonia is added. The precipitate is collected on a filter, washed first with dilute ammonia, then with water, and is next dissolved in warm dilute nitric acid (a small quantity of black residue sometimes remains insoluble), and the amount of silver thus obtained in solution is titrated with $N/10$ -ammonium thiocyanate solution; each c.c. of the latter solution is equivalent to 0.0014 gram of nitrogen. A second quantity of 100 c.c. of the filtrate is then treated with silver nitrate solution in the presence of an excess of potassium hydroxide; the precipitate formed is collected, and the nitrogen in it is estimated by Kjeldahl's method. The difference between the amounts of nitrogen found in the two estimations gives the nitrogen present in the form of dicyanodiamide.
W. P. S.

Estimation of Digitoxin in Foxglove Leaves and their Preparations. JAMES BURMANN (*Bull. Soc. chim.*, 1910, [iv], 7, 973-982).—It is now known that the three chief glucosides of foxglove leaves are digitoxin, digitalin, and digitonin, of which the first is of primary physiological importance and is the one usually estimated for medical purposes. Koller's method of estimation (*Abstr.*, 1898, ii, 267, 657) is that generally used, and a comparison has therefore been made between the amorphous digitoxin (ψ -digitoxin) isolated by this method of estimation and (a) crystalline digitoxin and (b) Cloetta's soluble digitoxin (digalene of commerce).

The results show that ψ -digitoxin and Cloetta's soluble digitoxin are both amorphous and are practically identical in melting point, solubility, and physiological activity, and that both are less active than crystalline digitoxin and show quite different physical constants.

Keller's process can only be regarded as useful in estimating the medicinal value of the drug and its preparations if it is admitted that in the product weighed there is a constant relation between the digitoxin and the other glucosides present.

T. A. H.

Estimation of Adrenaline in Normal Blood and after its Injection by means of Physiological Methods. PAUL TRENDLENBURG (*Arch. exp. Path. Pharm.*, 1910, 63, 171—176).—See this vol., ii, 971.

Estimation of Caffeine in Roasted Coffee. C. VIRCHOW (*Chem. Zeit.*, 1910, 34, 1037—1038).—Twenty grams of ground coffee are moistened with about 10 c.c. of water, and the mass is introduced into a shaking cylinder furnished with a stopcock and ground stopper. One hundred c.c. of chloroform are added, and the whole is well shaken for a minute. The chloroform is drawn off, and the extraction is repeated twice. To the united filtrate is added 1 gram of paraffin, and the chloroform is recovered by distillation. To the residue in the flask are then added 25 c.c. of hot water, the liquid is poured into a beaker, and the flask rinsed twice with 25 c.c. of hot water. The mixture is well stirred, then allowed to cool, and filtered; no caffeine is retained by the paraffin. On evaporating the aqueous solution, crude caffeine is left, which may be weighed. It is then purified by re-dissolving it in water, and again evaporating to dryness with addition of a little magnesium oxide and extracting the mass thrice with chloroform; on evaporating this, almost pure caffeine is left, but it is advisable by way of a check to ascertain its nitrogen content by means of a Kjeldahl estimation.

L. DE K.

Toxicological Detection of Colchicine. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1910, 63, 357—373).—Colchicine can in forensic cases be detected with certainty by a combination of chemical and biological tests. A slight modification is proposed in Zeisel's test. 1 mg. kills a white mouse. In frogs the toxicity of colchicine is increased 500-fold by warming them to 30—32°, and immunity can be produced in the usual way. In frogs, if the drug is introduced under the skin, it in part re-appears in the urine.

W. D. H.

Estimation of "Saccharin" in Urine. W. R. BLOOR (*J. Biol. Chem.*, 1910, 8, 227—232).—Methods previously proposed for the estimation of "saccharin" in the urine after its administration are not sufficiently exact when dealing with small quantities. The new method proposed is colorimetric and gives good results; the colour is due to the transformation of "saccharin" into what is probably benolsulphonaphthalein (sulphurein) by treatment with a phenol-sulphuric acid mixture, and is a bright yellow in weakly acid solutions, and purple-red in alkali. The purple fades after a time, but the yellow remains unchanged for a month or more. The test is performed with a benzene extract of the urine.

W. D. H.

Estimation of "Saccharin" in Urine and Fæces. ALFRED J. FAREMAN (*J. Biol. Chem.*, 1910, 8, 233—236).—The method is

practically the same as Bloor's (see preceding abstract), but differs in the apparatus used, in the employment of ethyl acetate instead of benzene as solvent, and in one or two other minor points. W. D. H.

Amylases. I. Examination of Methods for Determination of Diastatic Power. HENRY C. SHERMAN, E. C. KENDALL, and E. D. CLARK (*J. Amer. Chem. Soc.*, 1910, 32, 1073—1086).—A critical study of some of the methods in use for measuring diastatic power, carried out mainly on taka-diastase and pancreatin. The Lintner method is said to be insufficiently accurate for preparations of high diastatic power. A modified form of the iodine method is described, by means of which satisfactory results were obtained with taka-diastase, but not with pancreatin. Methods depending on the action of the latter enzyme on pure starch in pure water were found to be useless, because such a medium is too poor in electrolytes for the diastase to function normally. The optimum conditions necessary for the amylase to behave normally have been worked out and incorporated in a new gravimetric, copper-reduction method, which is described in detail. With commercial pancreatin this process gave results twenty times as high as when no electrolyte had been added. W. O. W.

Reaction Distinguishing between the Organic Derivatives of Arsenious Acid and Those of Arsenic Acid. ERCOLE COPELLI (*Boll. chim. farm.*, 1910, 49, 50—51. Compare Abstr., 1909, ii, 830).—The difference in stability towards reducing agents in alkaline solution which is shown by the above acids is shared by their organic derivatives. Atoxyl is reduced by nascent hydrogen in acid solution, giving a yellow precipitate, whilst in alkaline solution it is not attacked. The corresponding arsenious derivative, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_2 \cdot 2\text{H}_2\text{O}$, m. p. 90° , is prepared by treating atoxyl with sulphur dioxide in the cold, and precipitating with sodium carbonate. It is reduced by nascent hydrogen in alkaline solution (aluminium and potassium hydroxide), giving a yellowish-white precipitate, and also in acid solution, with formation of a sulphur-yellow precipitate. Methylarsinic acid, which is reducible in acid, but not in alkaline solution, yields when treated with sulphur dioxide a liquid which, when reduced with potassium hydroxide and aluminium, gives a yellow precipitate and blackens a test-paper impregnated with ammoniacal silver nitrate. R. V. S.

Characteristic Reactions of Atoxyl. QUINTO FIORI (*Boll. chim. farm.*, 1910, 49, 98—99).—Atoxyl yields an orange-red coloration with a solution of bleaching powder in the cold. Sodium methylarsinate and sodium cacodylate do not give this reaction, whilst antifebrin gives an olive-green coloration only when warmed. Mercuric chloride produces in solutions of atoxyl a white precipitate, which is soluble in dilute hydrochloric acid and in ammonia. Sodium methylarsinate gives with the same reagent a brick-red precipitate, which is also soluble in hydrochloric acid or ammonia, whilst acetaldehyde and the cacodylate yield no precipitate. The presence of arsenic in atoxyl can be shown readily after a preliminary fusion with sodium hydroxide. R. V. S.

General and Physical Chemistry.

Influence of Temperature on the Refractive Index of White of Egg. AMEDEO HERLITZKA (*Zeitsch. Chem. Ind., Kolloide*, 1910, 7, 251—256).—Previous observations relating to the influence of salts on the refractive index of egg-albumin are referred to. Contrary to the conclusions drawn by Frei (this vol., ii, 365), the author's data indicate that dissolved salts have no influence on the refractive index of colloids.

New measurements of the refractive indices of a series of solutions of egg-albumin have been made at temperatures between 7° and 47°. Whereas Frei's data led him to conclude that the refractive index of colloids varies with the temperature according to a linear equation, the author finds that a quadratic equation of the form $N_t = N_0(1 - K_1t - K_2t^2)$ is necessary for the representation of the temperature influence.

H. M. D.

Anomalous Dispersion of Light in an Aqueous Solution of Neodymium Nitrate. L. ISAKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 236—243 [Physical Part]).—Some preliminary experiments on the dispersion of neodymium nitrate by the interference method. A figure of the apparatus and a table and curves of the results obtained are given. The experimental results agree well with those calculated from the dispersion formula deduced.

Z. K.

Distribution of Chemical Elements in the Earth's Crust. VLADIMIR J. VERNADSKY (*Bull. Acad. Sci. St. Petersburg*, 1910, [vi], 129—1148).—The spectra of a large number of minerals have been investigated in the oxygen gas flame, and the results are given in series of tables showing which elements are present, numerous notes being added regarding the origin, nature, and so forth of the minerals and elements dealt with.

Indium, thallium, rubidium, caesium, gallium, and boron have been found for the first time in several minerals. In some natural glasses, bismuth, copper, and lead have been identified.

When the spectrum of indium is obtained by sparking a solution of a salt or a mineral containing the metal, the platinum wire continues to give the indium spectrum even after being repeatedly washed; the same phenomenon occurs with lithium; in the latter case it sometimes happens that a platinum wire which has ceased giving the lithium spectrum when dipped in pure water or acid, suddenly recommences to give the spectrum; this may possibly be due to the formation of some compound of lithium and platinum. Various methods of determining the spectra of elements are discussed.

Z. K.

Ultra-red Line Spectra. III. Accurate Measurement of Wave-lengths greater than 27,000 Å.-U. FRIEDRICH PASCHEN (*Ann. Physik*, 1910, [iv], 33, 717—738. Compare Abstr., 1909, ii, 630).—The experimental arrangement is described by means of which measurements of the wave-lengths of lines in the ultra-red spectra of lithium, sodium, potassium, rubidium, caesium, and thallium have been made. Observations relating to the ultra-red spectra of cadmium, aluminium, silver, helium, and mercury are also recorded. A special form of iron-constantan thermo-element suitable for use in such measurements is described.

H. M. D.

Ultra-red Line Spectra. (Spectra of Silver, Copper, Caesium, Rubidium, Strontium, Barium.) H. M. RANDALL (*Ann. Physik*, 1910, [iv], 33, 739—746. Compare preceding abstract).—Wave-length measurements in the ultra-red spectra between 8000 and 30,000 Å.-U. are recorded. The grating spectro-bolometer designed by Paschen was employed.

H. M. D.

Relative Duration of Spectral Rays Emitted by Magnesium Vapour in the Electric Spark. GUSTAVE A. HEMSALECH (*Compt. rend.*, 1910, 151, 668—671).—Kayser and Runge's series of nebular lines, in the magnesium spectrum, as well as Rydberg's series of nebular lines, have been studied by the method previously described (*Compt. rend.*, 1905, 141, 1227; 1910, 150, 1743). The relative intensity of the lines is given in tabular form, together with their relative duration at two capacities. The lines of the nebular series are the more sensitive to changes in capacity. The presence of impurities in the magnesium electrodes was rendered evident by the abnormal duration of the foreign lines. The method may be of value in detecting unknown impurities in analysis.

W. O. W.

Spectra of Anode Rays. OTTO REICHENHEIM (*Ann. Physik*, 1910, [iv], 33, 747—762).—Spectral observations have been made of the anode rays which are emitted by salts of the alkali and alkaline-earth metals. In the case of the alkali metals the spectra show lines of the principal and first subsidiary series, but no lines belonging to the second subsidiary series could be detected, even on the plates which were obtained with the longest possible exposure. In general, the anode ray spectra resemble the arc spectra so far as the relative intensity of the individual lines is concerned.

The anode ray spectra of the alkaline-earth elements are much simpler than the corresponding arc spectra. The spectra of all three metals are of the same type, and consist of a series of pairs of lines having the same difference in frequency, and, further, of a single line which bears no obvious relationship to the other lines. The isolated lines in the case of calcium and strontium are the flame spectrum lines, $\lambda = 4227$ and $\lambda = 4608$ respectively. On the other hand, the isolated line found in the case of barium is $\lambda = 6142$, whereas the flame spectrum line is $\lambda = 5536$.

The lines in the anode ray spectra were found to exhibit the Doppler effect, and the magnitude of this was measured in several cases. The various observations are discussed with reference to the

question of what are the carriers of the negative electrons which are responsible for the line spectra. The author considers that the carriers in the case of both the principal and subsidiary series of lines are positively charged ions in accordance with Stark's theory.

H. M. D.

Absorption and Inversion Phenomena in Luminous Hydrogen. AL. PFLÜGER (*Ber. Deut. physikal. Ges.*, 1910, 12, 719—724).—Polemical against Ladenburg (this vol., ii, 811). The results of the author's previous work are summarised. H. M. D.

Absorption Spectra of Sulphur Vapour at Different Temperatures and Pressures, and their Relation to the Molecular Complexity of this Element. J. IVON GRAHAM (*Proc. Roy. Soc.*, 1910, A, 84, 311—324).—The absorption spectra of sulphur vapour have been photographed at temperatures varying from 530° to 900°, and at pressures ranging from atmospheric down to 10 mm. of mercury. The records obtained at constant pressure over the above interval of temperature show that two distinct absorption spectra are present, and these are attributed to the molecular complexes S_8 and S_2 . The various photographs obtained at constant temperature and different pressures indicate that above 580° the S_8 molecules dissociate directly into the diatomic molecules, whereas at or below 520° dissociation takes place with the formation of molecules which are intermediate in complexity. The wave-lengths and frequencies of the bands which are due to the S_8 and S_2 molecules are tabulated.

The conclusions thus arrived at on the basis of spectroscopic evidence are in agreement with the views expressed by Preuner in explanation of the course of dissociation of sulphur vapour at 445°. H. M. D.

Absorption Spectra and Constitution of Benzene Derivatives. I. NICOLAI A. WALLASCHKO (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 751—805).—Curves and tables are given of measurements made of the absorption spectra of *o*-, *p*-, and *m*-hydroxy-, methoxy- and acetoxy-benzaldehydes, phenol, and benzaldehyde in aqueous and alcoholic solutions of various concentrations, and with and without the addition of hydrochloric acid; also for the sodium bisulphite derivatives of benzaldehyde, for anisole, acetoxyphenol, resorcinol monomethyl ether, guaiacol in alcoholic or aqueous solution, mixtures of benzaldehyde and some of its derivatives with chloroform, and for various mixtures of benzaldehyde and guaiacol in alcoholic solution. The results are discussed in detail.

All the ortho- and meta-derivatives give absorption spectra curves of the same type as benzaldehyde, the only difference between the various spectra being that some of the bands in some compounds are more developed than in others. The meta-spectra are intermediate between those of benzaldehyde and the corresponding ortho-compound, and are more readily changed by the addition of hydrochloric acid to the alcoholic solution, the effect being to make the spectra approach nearer to that of phenol. The reason for this is the formation of the unstable compound, $OH \cdot C_6H_4 \cdot CHCl \cdot OH$, which becomes hydrolysed on greater dilution. In water, this compound is

completely hydrolysed, consequently the addition of hydrochloric acid to an aqueous solution of the compounds has no effect. (On the other hand, the ortho-benzaldehyde derivatives in aqueous solution are similarly affected by the addition of sodium hydrogen sulphite, and the greater the concentration of the latter, the more do their spectra approach that of phenol.

The *p*-hydroxy- and -methoxy-derivatives in acid and neutral alcoholic or aqueous and in chloroform solution give curves of the same type as phenol, but the spectra of the *p*-acetoxy-derivative is more like that of *o*-hydroxybenzaldehyde.

The introduction of the benzaldehyde group into the benzene ring induces a definite new state of the latter, and this effect is strengthened by the introduction in the ortho- or meta-position of an acetoxy-, methoxy- or hydroxy-group; these groups are, therefore, regarded as auxo- or batho-chromes, the influence of which on the spectra is to move the absorption bands from the violet towards the red end of the spectrum. A similar effect is produced by the acetylation of benzaldehyde in the para-position, the effect being the same as the acetylation of phenol, which greatly decreases the influence of the hydroxyl group on the benzene ring, but the hydroxy- or methoxy-group in the para-position decreases greatly the influence of the aldehyde group on the benzene ring, but has no influence on the hydroxyl group in phenol, consequently the spectra differs little from that of the latter. The absorption spectrum of a mixture of benzaldehyde and phenol in equimolecular proportions is very much like that of *p*-acetoxybenzaldehyde. A study of the complex curves obtained by mixtures of substances leads the author to reject Baly and Collie's explanation (Trans., 1905, 87, 1332) of the benzaldehyde spectrum. On the contrary it is maintained that benzaldehyde has a greater selective absorption than phenol, and that the entrance of the aldehyde group does not retard the internal motion of the benzene, but induces a new form of vibration. The general results and conclusions drawn from the study of complex absorption spectra agree with those of Hartley (Trans., 1909, 95, 52). Z. K.

Progressive Phosphorescence at a Low Temperature. JOSEPH DE KOWALSKI (*Compt. rend.*, 1910, 151, 810—812).—The fluorescence of some aromatic compounds in alcoholic solution has been examined at different temperatures between -100° and -190° . At about -135° the solutions were viscous, the fluorescence extended towards the red, and was apparent even when not visible at the ordinary temperature. In the case of phenanthrene, anthracene, and others, the fluorescence terminated in the ultra-red. Fluorescence was observed below -135° , when the solutions solidified, whilst at -150° to -165° phosphorescence also appeared, the duration of the latter increasing as the temperature was lowered. A progressive phosphorescence was also observed, having an emission spectrum characteristic for the substance in solution, but independent of the temperature. The bands of which it was composed were more intense and persistent than the broad bands due to ordinary phosphorescence, which disappears as soon as the light exciting it is removed.

For each substance there was a definite temperature above which progressive phosphorescence did not appear. This temperature limit appears to be independent of the freezing point or electrical conductivity of the solution. Phenanthrene does not show the phenomenon above -158° .

W. O. W.

Rotation Dispersion. II. HERMANN GROSSMANN and BERNHARD LANDAU (*Zeitsch. physikal. Chem.*, 1910, 75, 129—218. Compare Abstr., 1909, ii, 713; this vol., ii, 563).—The optical rotation of methyl *l*-malate in over ninety solvents in different dilutions has been measured at 20° for red, yellow, green, light blue, dark blue, and violet light by the method already described (*loc. cit.*), and a number of measurements have also been made with ethyl *d*-tartrate. Methyl malate is specially advantageous for such measurements, owing to the fact that the dispersion curve of the pure liquid is normal, as the following figures show:

| Light. | Red. | Yellow. | Green. | Light blue. | Dark blue. | Violet. |
|-------------------|-------|---------|--------|-------------|------------|---------|
| $[\alpha]_D^{20}$ | -5.62 | -6.42 | -7.57 | -8.96 | -9.49 | -9.83 |

The dispersion curve of methyl tartrate is abnormal. For full details as to the magnitude and sign of the rotation in the different solvents in varying dilutions, the original paper must be consulted.

The more important general conclusions with reference to the action on methyl malate are as follows. In organic solvents containing halogens (over thirty such solvents were used) there is a tendency to reverse the direction of the rotation. This tendency attains its maximum when there are four chlorine atoms in the molecule; it is less when five chlorine atoms are present. Bromal, chloral, and acetyl chloride have an effect different from that of the other halogen compounds, which is accounted for by the fact that the solutions show mutarotation. Further, in most cases the rotation attains a maximum in these solvents and then diminishes somewhat, and the final value is attained only after four or five days. Somewhat similar results are obtained with ethyl tartrate. Heat is developed when the esters are dissolved in the above three solvents, so that the mutarotation is doubtless connected with chemical combination, but this does not account for the maxima.

The effect of solvents containing a hydroxyl (including carboxyl) or nitro-group is similar to those containing halogens, but solvents containing a free amino-group or a nitrogen in the ring of a heterocyclic compound markedly increase the levorotation of the ester. That the effect just described is due to these groups is supported by the observation that when the hydroxyl or amino-group is modified by putting in alkyl or other groups, the influence on the rotation is lessened or non-existent. The methyl group, as shown by observations with hydrocarbons and fatty acids, also has a tendency to reverse the sign of the rotation. Solutions in formic acid showed mutarotation, and detailed observations on this phenomenon were made. In contrast to other groups, the aldehyde group in aliphatic compounds markedly increases the levorotation of the ester. The same group in aromatic compounds has a similar but less pronounced influence.

As regards isomeric compounds, examples are given where a group in the meta-position has a greater influence on the rotation than when in the ortho-position. The difference in the effect of a group when in the nucleus and side-chain was analogous in all cases; the effect is greater in the latter position.

As inorganic solvents, water, sulphuric acid, arsenic trichloride, phosphorus trichloride, and phosphoryl chloride were used, and measurements with both active esters were made. Water has very little effect on the specific rotation of methyl malate. The two halogen compounds of phosphorus cause rotation to the left with both esters. Methyl malate shows mutarotation in phosphoryl chloride, but ethyl tartrate does not. Of all the solvents examined, arsenic trichloride has the greatest effect in reversing the rotation. In the violet, the specific rotation of ethyl tartrate is -39.64 , of methyl malate $+29.68$. In sulphuric acid the natural rotation of the esters is considerably increased.

The observations show that anomalous rotation dispersion is by no means a rare phenomenon; it occurs in each case where the solvent has a tendency to reverse the direction of rotation of the solute.

The influence of concentration on rotation is also discussed. G. S.

Measurement of the Rotation Dispersion of Optically Active Compounds by means of the Nernst Light. HERMANN GROSSMANN and BERNHARD LANDAU (*Zeitsch. Ver. deut. Zuckerind.*, 1910, 1109—1117).—The use of a Nernst lamp in combination with suitable light filters is recommended for the measurement of rotation dispersion. The rotation produced by a 1-millimetre quartz plate has been determined for the approximately monochromatic light which is obtained by use of the coloured solutions suggested as filters by Landolt and by Winther. The specific rotations of dimethyl *l*-malate and diethyl *d*-tartrate for the various coloured rays are recorded, and diagrams are given showing the influence of the solvent on the rotation dispersion of these substances in solution (see preceding abstract). H. M. D.

Liquids with Conical Focal Lines. GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.*, 1910, 151, 762—765. Compare this vol., ii, 803).—A geometrical description and discussion of the appearances presented by anisotropic liquids of the type of ethyl azoxybenzoate when these are viewed between crossed nicols under the microscope.

W. O. W.

Triboluminescence. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Petersburg*, 1910, [vi], 1037—1041).—The property of triboluminescence of substances is closely associated with their electric properties; thus where triboluminescence occurs in substances having a centre of symmetry, pyroelectric and other electric properties also occur. Triboluminescence is a surface phenomenon, and temporary triboluminescence is due to the change in the physical properties of the surface of the crystal. Z. K.

The Nature of Triboluminescence. IWAN VON OSTROMISLENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 591—606. Compare preceding abstract).—A large number of substances, chiefly organic compounds, investigated by the author and others are tabulated with respect to their triboluminescence, and the following conclusions are drawn. If one member of a group of chemical compounds which form solid solutions with one another, or with some common substance, is permanently triboluminescent, then all the other members will be permanently triboluminescent.

An apparent exception occurs in a group of substances forming solid solutions with dibenzyl, but the latter is shown to occur in two modifications, of which the β -modification and the substances forming solutions with it are not luminescent. A permanently triboluminescent crystal does not give solid solutions with non-luminescent substances, and if one component of a solid solution is triboluminescent, then the solution is likewise triboluminescent.

The triboluminescence of a substance depends only on the system and structure of its crystals; it depends on its chemical constitution only so far as the latter influences crystalline form. Racemic mixtures of triboluminescent substances are always non-luminescent; apparent exceptions are probably not racemates, but only physical mixtures of the two compounds, or they may be cases of temporary luminescence; on the other hand, optically inactive compounds of such type as mesotartaric acid may be triboluminescent.

Only substances the crystals of which have no centre of symmetry can possess the property of permanent triboluminescence. Exceptions to this rule observed by Vernadsky and others are either cases of temporary luminescence (for in some cases the decay of this property may take a very long time), or the crystalline form of the substance in question has not yet been accurately determined. Thus at 130°, potassium nitrate, which at that temperature exists as hexagonal crystals of the rhombohedral class, is permanently triboluminescent, but at the ordinary temperature, when the crystals belong to the rhombic system of the holohedral class, they are only triboluminescent when freshly prepared. There is also reason to think that the intensity of triboluminescence depends on the system and class to which the crystals of a substance belong.

Z. K.

Triboluminescence of Racemic Compounds. IWAN VON OSTROMISLENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 607—609. Compare preceding abstract).—The fact that racemic compounds are never triboluminescent can be used as a very rapid, simple method of distinguishing between the racemate and the mere mixture of two optically active compounds, and also to ascertain the exact point at which a racemate is resolved into its constituents and vice versa. This method may also be employed to determine exactly when one non-triboluminescent modification of a substance passes into a new crystalline, triboluminescent modification.

Z. K.

Triboluminescence of Minerals. B. A. LINDNER (*Bull. Acad. Sci. St. Petersburg*, 1910, [vi], 999—1022).—A historical résumé of

the previous work done on the subject. The triboluminescence of various natural minerals has been examined, and the minerals are classified with respect to this property and their chemical constitution. The following conclusions are drawn: (1) Triboluminescence in organic substances is of frequent occurrence. (2) Whereas the triboluminescence of artificial crystals is sometimes only temporary, that of the natural crystals is constant, and does not depend on the time. (3) Minerals belonging to the most varied chemical classes and groups can show the property, but with few exceptions either all or none of the members of an isomorphous series are triboluminescent. (4) The hardness of a mineral exercises no influence, but the more brittle and the more marked the cleavage the more intense is the luminescence. (5) All triboluminescent minerals are non-conductors of electricity, and all those that have pyroelectric properties are also triboluminescent. The character of the luminescent sparks is the same for all minerals. (6) The triboluminescence does not depend on the character and temperature of the medium surrounding the mineral. After reviewing the various theories advanced to explain triboluminescence, the author draws the conclusion that the most applicable is Vernadsky's (*Bull. Acad. Sci. St. Petersburg*, 1906, 49), namely, that the triboluminescence of chemical compounds is closely dependent on their crystalline form. So far as is at present known, the crystalline form of nearly all triboluminescent substances belongs to the class in which there is no centre of symmetry. Z. K.

Oxidation of Hydrogen Iodide under the Influence of Light. B. S. SCHWEZOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 219 [Physical Part]).—The purpose of the research was the construction of a chemical photometer. The oxidising action of sulphuric, hydrochloric, and nitric acid on potassium iodide in diffused sunlight was investigated in a special apparatus, of which a figure is given. A constant current of air passing through the mixture kept the concentration of oxygen in it constant. Nitric acid reacts rapidly even in the dark; sulphuric and hydrochloric acid react much more slowly, and with about the same velocity. The order of reaction, calculated by the formula

$$n = (\log Q - \log Q_2) / (\log C_1 - \log C_2)$$

(Q and Q_2 = concentration of the separated iodine; C_1 and C_2 the concentration of potassium iodide) is 2 for dilute solution, and 2.25 for concentrated solutions (compare Plotkinoff, *Abstr.*, 1907, ii, 212; 1908, ii, 790). Equivalent quantities of sodium, potassium, and cadmium iodide under similar conditions evolve equal quantities of iodine. Z. K.

Chemical Changes Produced by Different Kinds of Rays
IV. Catalytic Action of Sunlight in the Presence of Inorganic Substances. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, 29, 279—293. Compare *Abstr.*, 1908, ii, 915).—The author summarises the chemical changes already investigated when various substances are exposed to sunlight in the presence of uranium salts. He now shows that various other inorganic substances exert a similar action, and gives the qualitative results of the exposure of solutions of forty-five different substances in the presence of ferric sulphate. Most of these substances show changes of degradation. Certain reactions were also

quantitatively investigated. In the case of alcohols, the amount of aldehyde formed was estimated; in that of α -amino-acids and peptones, the amount of ammonia evolved in deamidisation; in that of β -amino-acids, the amount of amino-aldehyde formed. In the case of *l*-glucose, the diminution of fermentable sugar was estimated, and in those of the disaccharides, the amount of inversion. The amount of uric acid destroyed was also estimated, and also the amount of phosphoric acid set free from nucleic acids, and the amount of salicylic acid formed from benzoic acid.

S. B. S.

Photo-electric Experiments with Anthracene. WALTER STEUBING (*Ber. Deut. physikal. Ges.*, 1910, 12, 867—868).—A reply to criticism on the part of Byk and Borck (this vol., ii, 814) of previous experiments by Stark and Steubing (*Abstr.*, 1908, ii, 746) on the photo-electric sensitiveness of anthracene. The experimental arrangement employed is described, and reasons are advanced in support of the validity of the conclusion that anthracene is photo-electrically active.

H. M. D.

Nature of the Ionisation Produced by α -Rays. FRANK E. WHEELLOCK (*Amer. J. Sci.*, 1910, [iv], 30, 233—255).—Experiments have been made to test whether columnar ionisation affords a complete explanation of the lack of saturation obtained in α -ray ionisation when moderate fields are employed, or whether "initial re-combination" also plays any part. With a perpendicular field, the lack of saturation is less than with a parallel field, as Moulin found (*Abstr.*, 1908, ii, 921). The ratio of two currents obtained with a constant field and two sources of α -rays differing in intensity does not depend on the field when it is parallel to the path of the rays, but does when it is perpendicular, as though with strong currents the ions in different columns interspersed with one another. A theoretical expression based on the hypothesis of columnar ionisation gave a saturation curve different from the experimental, saturation being approached, as the field increases, more slowly than the expression required. On this and other data, the conclusion is drawn that possibly both the hypotheses of columnar ionisation and of initial re-combination may be necessary to explain all the peculiarities of α -ray ionisation.

F. S.

Absorption and Reflexion of the β -Particles by Matter. ALOIS F. KOVARIK (*Phil. Mag.*, 1910, [vi], 20, 849—866).—The radioactive substances employed, radium-*D* and -*E*, actinium-*C'*, radium-*B*, thorium-*A*, -*B*, -*C*, and -*D*, were deposited on very thin aluminium leaf the absorption and scattering of which is negligible. Such preparations covered directly with thin aluminium foil and placed some distance below the electroscope, give an absorption curve showing an increase in the ionisation for the first 0.05 to 0.01 mm. of aluminium, or equivalent thickness of tin, which is ascribed to scattering. When the distance of the absorbing foils from the preparation was increased, the maximum decreased in magnitude, until finally the reverse effect, studied by Crowther, showed itself. In a hemispherical ionisation chamber, arranged so that the path of all rays was the same, it was shown that

the rays reflected from the support beneath the preparation were always less penetrating than the direct rays, the less so the greater the atomic weight of the reflector. Measurements of the absorption coefficients of the various rays were taken with as much aluminium below as above the preparation to compensate for reflexion. The curves obtained were very nearly exponential.

For different β -rays the percentage of the radiation reflected increases with increase in the velocity of the rays and with the atomic weight of the reflector. For very penetrating β -rays [$\lambda(\text{cm.})^{-1}$ above 20], however, the percentage reflected again decreases. By multiple reflection from the sides of the ionisation chamber, the ionisation may be increased three and a-half times.

F. S.

The Reflexion of Homogeneous β -Particles of Different Velocities. ALOIS F. KOVARIK and W. WILSON (*Phil. Mag.*, 1910, [vi], 20, 866—870).—The β -rays of radium C, from a sealed bulb of radium emanation, were sorted out into homogeneous rays by a magnetic field, and entered a flat ionisation chamber, made of thin aluminium leaves, which could be inclined at different angles to the rays, and could be covered with reflecting substances. It was found that the power of substances to reflect the rays increased with the velocity of the rays, from $H\rho=1000$ to $H\rho=\text{about } 3000$, and then slightly decreased again, but the ratio of the reflective powers of lead and copper was the same whatever the velocity of the rays.

F. S.

The Heterogeneity of β -Rays from a Thick Layer of Radium-E. J. A. GRAY and W. WILSON (*Phil. Mag.*, 1910, [vi], 20, 870—875).—Using a thick layer of radium-D and -E, it was found that, although the whole radiation was absorbed exponentially [$\lambda(\text{cm.})^{-1}=43$] by aluminium, different bundles of rays of widely different penetrating power [$\lambda(\text{cm.})^{-1}$ from 13 to 62.5] could be sorted out by a magnetic field. When the rays had first to pass through aluminium, it was proved by magnetic deflexion measurements that the average velocity of the rays surviving was increased.

F. S.

The Deflexion by an Electrostatic Field of Radium-B on Recoil from Radium-A. SIDNEY RUSS and WALTER MAKOWER (*Phil. Mag.*, 1910, [vi], 20, 875—882).—Some, at least, of the atoms of radium-B recoiling from radium-A are positively charged, although in the disintegration of radium-A positively charged α -rays are also expelled. The "recoil atoms" from a wire made active by a deposit of radium-A were passed between oppositely charged plates in a vacuum and fall upon a metal cross-piece. The distribution of the activity on the latter was determined by moving it under a narrow slit in the base of an α -ray electroscope. The point of maximum distribution was shifted by the application of a field to the plates, and from the magnitude of the shift the charge carried by the "recoil atoms" was deduced, on the assumption that the velocity of the atoms was 3.27×10^7 cm. per second, which is that calculated from the principle of equality of momentum of the two parts of a disintegrating atom.

The values obtained indicated that the recoil atom carries unit positive charge, and that its mass is 214, in agreement with what is to be anticipated from the disintegration theory.

F. S.

The Deflexion by a Magnetic Field of Radium-*B* on Recoil from Radium-*A*. WALTER MAKOWER and E. J. EVANS (*Phil. Mag.*, 1910, [vi], 20, 882—886).—Similar experiments to those described in the preceding abstract were carried out, the "recoil atoms" being deviated in a magnetic instead of an electrostatic field. The distribution of the activity on the cross-piece was determined by laying it on a photographic plate, and then measuring the photograph obtained by projecting it on to a screen by means of a lantern. The value for $H\rho$ of the deflected "recoil atoms" was 6.52×10^5 . This is twice that obtained by Rutherford for the α -particle of radium-*A*, and, since $H\rho = mv/e$, and the value of mv must be the same in both cases on the principle of equality of momentum, it follows that the charge carried is the unit charge instead of twice the unit charge, as in the case of the α -particle. By combining the results of the electrostatic and magnetic deflection measurements, it follows that the velocity of the "recoil atom" is 3.23×10^7 , and its mass is 194 ($H=1$), which is as close to the theoretical value 214 as can be expected.

F. S.

Measurements of the Rate at which Helium is Produced in Thorianite and Pitchblende, with a Minimum Estimate of their Antiquity. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, A, 84, 379—388).—A description is given of the methods employed to measure the rate of production of helium from solutions of thorianite (two varieties, one specially rich in uranium from the Galle district of Ceylon) in nitric acid, and of pitchblende. The latter was dissolved in nitric acid, and the insoluble sulphates converted into carbonates and dissolved to form a separate solution. The solutions were contained in large flasks closed by barometer tubes dipping beneath mercury, and the gaseous contents were removed periodically with steam by boiling the liquids. The volume of helium was estimated in the expelled gas after subjection to cooled charcoal in a narrow capillary tube. The rate of production of helium per gram of mineral per annum was found to be $3.7 (\times 10^{-8})$ c.c. for Galle thorianite, containing 24.5% of U_3O_8 and 65.44% of ThO_2 ; 2.79 for ordinary thorianite, containing 13.10% of U_3O_8 and 72.65% of ThO_2 ; and 3.16 for pitchblende, containing 37.6% of U_3O_8 . These results are in good agreement with those calculated earlier on certain assumptions. The minimum ages of the two thorianites are 2.50 and 2.80 ($\times 10^{-8}$ years) respectively, as calculated from the period required to produce the contained helium, no allowance being made for the helium that escapes. The minimum ages of 4 minerals previously worked with are, in millions of years, (1) sphærosiderite (Oligocene) 8.4, (2) hæmatite (Eocene) 31, (3) hæmatite (Carboniferous limestone) 150, (4) sphene (Archean) 710.

F. S.

Disengagement of Emanation from Radium Salts. III. LÉON KOLOWRAT (*Le Radium*, 1910, 7, 266—269. Compare this vol., ii, 31).—With barium chloride containing only minute proportions

of radium chloride, the disengagement of emanation from the salt at a temperature θ , after a period of accumulation t from the moment of complete removal of emanation by fusing the salt, is the same whether the temperature is maintained at θ throughout or for only a short time at the end of the period of accumulation, and is represented by $c(1 - e^{-\lambda t})/\lambda$, where λ is the constant of the emanation, and c a coefficient between 0 and 1, which is a function of θ , but independent of t ; c may be considered as the fraction of the emanation generated retained by the solid salt at θ , and may be determined with consistency in different experiments at the one temperature for different times for the same preparation, but varies greatly with different preparations otherwise apparently similar. Impure preparations seem to have lower values of c than those only containing barium and radium chloride. The idea that part of the radium chloride is in the form of a solid solution in the barium chloride and gives up its emanation more readily than the rest supposed to be present with the barium chloride in the form of mixed crystals (Kolowrat, this vol., ii, 767) does not account for the differences, as there is no regular relation between the value of c and the proportion of radium present. Using a few thousandths of a milligram of pure radium chloride, it was found that heating to the fusion temperature no longer effected complete release of the accumulated emanation, the material being changed by high temperature into an insoluble and probably infusible product. This agrees with Mme. Curie's observation that heating reduces the escape of emanation from radium chloride, and was confirmed by observations on the minimum β -radiation attained by the preparations after heating. The 1% barium-radium chlorides are less easily changed by heat, and give up the whole of their contained emanation by fusion.

F. S.

Action of Radium Emanation on Colloids. WILLEM P. JORISSEN and H. W. WOUDESTRA (*Chem. Weekblad*, 1910, 7, 941-948. Compare Henri and Mayer, Abstr., 1904, ii, 184).—The authors confirm the results obtained by Henri and Mayer in their work on the action of radium emanation on colloids. They find that the sensitivity of a colloid towards an electrolyte is increased by this emanation.

A. J. W.

The Diffusion of Gaseous Ions. ÉDOUARD SALLES (*Compt. rend.*, 1910, 151, 712-714).—The coefficients of diffusion of ions in carefully dried air, carbon dioxide, nitrogen, and oxygen, produced by the α -rays of polonium, have been measured by a method the principle of which is due to Townsend. The values are in accord with those given by Townsend for ions produced in other ways, the positive ion for oxygen ($k=0.030$) being the only one in disagreement. Experiments under pressure p (mm. of mercury) showed for $p \times k$ constant values of about 22 for the positive, and 32 for the negative, ions in air and nitrogen.

F. S.

Attempts to Prepare Metallic Radium. ERICH EHLER (*Ber.*, 1910, 43, 2613-2618).—From 0.02 gram of barium bromide con-

containing 2.5% of radium bromide, about 1 mg. containing 9% was prepared by crystallisation, converted into carbonate, and dissolved in aqueous hydrazoic acid. On evaporation, a white, crystalline mass of radium azoimide, $\text{Ra}(\text{N}_3)_2$, containing barium azoimide was left. Previous experiments with barium azoimide had shown that it is not decomposed by the action of radium rays. The preparation was brought into a narrow "melting-point tube," supported inside a perfectly exhausted glass tube, and heated in a special sand-bath very slowly to $180-250^\circ$. After some hours, a shining metallic mirror was formed, which was sealed off from the preparation, and found to contain 73% of the radium employed, by electroscopic measurements. The radium mirror was dissolved out of the tube and converted into chloride. In spite of the impurity of the preparation, the experiment proves that elementary radium is chemically and physically analogous to elementary barium. It appears to form nitride with moist air even more readily than barium.

F. S.

The Radium Content of Waters of the Cam, Cambridge Tap Water, and Some Varieties of Charcoal. JOHN SATTERLEY (*Proc. Camb. Phil. Soc.*, 1910, 15, 540-544).—The emanation generated per litre of Cambridge tap water and of Cam river water respectively is that in equilibrium with 130 and 5 ($\times 10^{-12}$ gram of radium), while the amount of radium is 1.6 and 3.2 ($\times 10^{-12}$ gram). The Cambridge waters are therefore richer in radium than those of Montreal, which accounts for the higher values found for the quantity of emanation in the air of Cambridge than in that of Montreal. In four varieties of charcoal, the radium contents per gram were: (1) cocoanut 0.4, (2) cocoanut 0.3, (3) Brazil-nut 1.3, (4) wood 0.3 ($\times 10^{-12}$ gram).

F. S.

Investigations on the Radium Content of Rocks. I. ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 359-365).—The investigation includes ten rocks from the West Coast of Sumatra, comprising quartz porphyrite, granite, basalt, andesite, augite-andesite, granitite, diorite, and diabase. These rocks showed a content of radium of the order of 10^{-12} gram per gram, similar in magnitude to those which have been examined by other investigators. The highest was a basalt from the volcano of Asar (13.0), and the lowest were the diorite and diabase (0.3×10^{-12} gram of radium per gram).

F. S.

The Radium Content of Basalt. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, A, 84, 377-379).—The discrepancy between the author's results and those of Joly on the radium content of igneous rocks is greatest in the case of basalts, the value found by the latter being about eight times that found by the former. New measurements with special precautions have therefore been made on a new set of three basalts, which give results even lower than the previous set (from 0.16 to 0.35×10^{-12} gram radium per gram), whilst in one sample previously employed a new determination gives the same result as before (0.57). It is possible that Joly has met with exceptional specimens.

F. S.

The Presence of Radioactive Elements in Some Incrustations from the Fumaroles of Vesuvius. GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iia], 16, 48—50. Compare Abstr., 1907, ii, 365).—Incrustations from recent fumaroles, dissolved in hydrochloric acid and precipitated with hydrogen sulphide, yield a mixture of sulphides, from which, after removing arsenic by ammonium sulphide, boiling with dilute hydrochloric acid, and dissolving in nitric acid, lead is removed as sulphate, and a greyish-white precipitate is then obtained by the addition of ammonia. This precipitate is markedly radioactive. C. H. D.

The Radioactivity of the Products of the Recent Eruption of Etna. ARNALDO PIUTTI and GENNARO MAGLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iia], 16, 159—163).—The products of the recent volcanic eruption of Etna have been studied in the same manner as those of Vesuvius (this vol., ii, 290). The smallest radioactivity is possessed by the volcanic sands, followed in ascending order by the lava, the scorie, and the sublimed products and incrustations. The maximum activity agrees with that of the materials obtained from the preceding eruption, and is greater than that of corresponding materials from the last eruption of Vesuvius, in which, however, the same relative order is observed. C. H. D.

Radioactivity of Italian Minerals. RAFFAELLO NASINI and MARIO G. LEVI (*Gazzetta*, 1910, 40, ii, 101—122. Compare Abstr., 1909, ii, 7, 110).—A complete account of the work on this subject carried out by the authors and others. R. V. S.

A Determination of the Ratio of Mass to Weight for a Radioactive Substance. L. SOUTHERNS (*Proc. Roy. Soc.*, 1910, A, 84, 325—344).—The ratio of mass to weight of the oxides of lead and of uranium have been compared by filling the hollow bob of a specially constructed rigid pendulum with these two substances, and no difference between them has been indicated. The ratio is the same for the two substances within one part in 200,000. F. S.

Electrical Purification and Conductivity of Liquid Sulphur Dioxide. J. CARVALLO (*Compt. rend.*, 1910, 151, 717—719).—When a current is passed through liquid sulphur dioxide free from air between platinum electrodes, the difference of potential being V , it is found that the current I diminishes with time until a limit is attained. The negative electrode becomes slightly brown, and the liquid undergoes purification by prolonged passage of the current.

When V is 200—500 volts, the limiting current does not vary as a simple function of V . With a difference in potential of 1000 or 2000 volts, the current is much smaller than that passing with lower tensions. Curves plotted for $I=f(V)$ are in accordance with Ohm's law, when V does not exceed 100 volts. The limiting conductivity for higher voltages is not in agreement with this; the law governing it under these conditions appears to resemble the laws for the conductivity of gases, and will be further studied. The limiting specific

resistance under 100 volts was 7.6×10^9 ohms; under 2350 volts, 4.9×10^{10} ohms, and under 4000 volts, 4.9×10^{10} ohms per cm.

W. O. W.

Electrical Conductivity of Solutions in Aniline, Methyl-aniline, and Dimethylaniline. AL. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 683—690).—The object of the research was to determine the connexion between the chemical nature of an amine and its dissociating power and its power of giving conducting solutions. Since the dielectric constants of the three amines are very close to one another, any difference that may exist in their dissociating powers would be due to the difference in their chemical constitutions. The following salts were employed: ammonium iodide, pyridine hydrobromide, aniline hydrobromide, silver nitrate, and lithium iodide, and tables and a curve for aniline solutions are given, showing the relation of concentration to electrical conductivity. All the solutions show a rapid diminution of their molecular electrical conductivity with increasing dilution, this probably being due to the formation and dissociation of complex salts, such as $\text{NH}_4\text{I}, 2\text{PhNH}_2$, $\text{AgNO}_3, 2\text{PhNH}_2$. Aniline gives the best conducting solutions, methylaniline comes next, whilst the solution in dimethylaniline seems to be on the border between conducting and non-conducting solutions. The conclusion is drawn that the chief factor determining the ability to give conducting solutions is the chemical constitution of the amine.

Z. K.

The Potential of the Sodium Electrode. GILBERT N. LEWIS and CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1910, 32, 1459—1468).—A method of obtaining the difference of potential between metallic sodium and a solution of sodium ions of normal concentration is described. This consists in determining the potential difference between a dilute sodium amalgam and an aqueous solution of sodium hydroxide, and also the *E.M.F.* of the cell metallic sodium | sodium iodide dissolved in ethylamine | sodium amalgam. The *E.M.F.* of this galvanic combination is independent of the medium in which the sodium salt is dissolved, and ethylamine was chosen because it is not acted on by the alkali metal.

The *E.M.F.* of the combination sodium amalgam (0.206% sodium) | 0.2*N*-sodium hydroxide | normal calomel electrode was found to be 2.1986 volts. Assuming that the sodium hydroxide is ionised to the extent of 82.8%, this gives for the *E.M.F.* of the cell sodium amalgam | aqueous solution containing Na ions in normal concentration | normal calomel electrode, 2.1525 volts. The potential difference between sodium and 0.206% sodium amalgam is 0.8456 volt, and these data when combined give for the *E.M.F.* of the combination sodium | aqueous solution containing 1*N*-sodium ion | normal calomel electrode, 2.9981 volts at 25°.

The temperature-coefficient of the sodium-sodium amalgam cell is -0.0000408 volt per degree, and from this it is calculated that the heat of solution of 1 gram-atom of sodium in 0.206% sodium amalgam is 19,790 cal.

The precautions to be observed in the preparation of pure sodium

amalgam and of anhydrous ethylamine are described in detail. If these are followed, the observed potential differences can be reproduced with great accuracy.

H. M. D.

Oscillographic Investigation of Some Electrolytic Processes.

III. D. REICHSTEIN (*Zeitsch. Elektrochem.*, 1910, 16, 916—944. Compare Abstr., 1909, ii, 960).—Using a more sensitive oscillograph (on the photographic record a deflexion of 1 mm. on the ordinate axis is given by a current of 0.0004 ampere, whilst 1 mm. on the axis of abscissae corresponds with 0.0006 second), the author has studied the polarisation of an electrode produced by a fairly strong current lasting a few hundredths of a second and its subsequent decay. The cases examined are the anodic and cathodic polarisation of platinum (also mercury and silver) in 28% sulphuric acid; the anodic polarisation of copper, silver, lead, and nickel in solutions of their salts, and the cathodic polarisation of palladium in sulphuric acid and in acid zinc sulphate. In all the experiments the experimental electrode is combined with a large, unpolarisable electrode. The results are, as a rule, given in the form of reproductions of the oscillograph curves. The main result, however, is that during the passage of the polarising current, the difference of potential between the electrode and the solution is always much larger than the equilibrium *P.D.* when no current is flowing, and the difference increases with the current. The rate of disappearance of this excess depends on the nature of the product of electrolysis and of the electrode. The phenomenon is met with in every case examined; it is hardly possible to give the details, and also the possible mechanisms which the author suggests in explanation of them in a brief abstract. It may be said, however, that the view is taken that the primary products of the electrolysis are not identical with the stable substances finally formed, the decay of the excess polarisation being due to the transformation of one into the other. T. E.

The Potentials of Chlorine, Bromine, and Iodine in Methyl and Ethyl Alcohol. J. NEUSTADT (*Zeitsch. Elektrochem.*, 1910, 16, 866—869).—The *E.M.F.* of a cell $\text{Ag} | \text{saturated solution of AgCl} | \text{Cl}$ is independent of the solvent used. It is given by $E = \epsilon_{\text{Ag}} - \epsilon_{\text{Cl}} + RT/nF(\log[\text{Ag}'] + \log[\text{Cl}'])$. The quantity in the brackets is the logarithm of the solubility product of silver chloride, and ϵ_{Ag} and ϵ_{Cl} are the normal potentials of silver and chloride in the solvent used. From the value of *E* for aqueous solutions and determinations of the solubility products of the silver haloids in the alcohols, the differences of the normal potentials of the haloids in alcoholic solutions are therefore easily calculated. The solubility products in alcoholic solutions are obtained by measurements on concentration cells of the type $\text{Ag} | 0.1N\text{-AgNO}_3 | 0.1N\text{-KCl saturated with AgCl} | \text{Ag}$. The concentrations of the silver and chlorine ions in the alcoholic solutions are calculated from the conductivity measurements of Deimpf (Abstr., 1905, ii, 9). The mean values of the solubility products at 25° are:

| | Methyl alcohol. | Ethyl alcohol. |
|------------|------------------------|------------------------|
| AgCl | 1.95×10^{-13} | 1.85×10^{-14} |
| AgBr | 1.1×10^{-16} | 6.4×10^{-16} |
| AgI | 1.5×10^{-18} | 1.1×10^{-17} |

The differences of the normal potentials, calculated in the way indicated above, are :

| | Water. | Methyl alcohol. | Ethyl alcohol. |
|--|--------|-----------------|----------------|
| $\epsilon_1 - \epsilon_{\text{H}_2\text{O}}$ | 0.467 | 0.418 | 0.471 |
| $\epsilon_1 - \epsilon_{\text{Et}}$ | 0.772 | 0.707 | 0.712 |

Determinations in acetone were impossible, owing to formation of complex salts. T. E.

Heat Development of the Clark Cell. F. POLLITZER (*Zeitsch. physikal. Chem.*, 1910, 74, 748).—Cohen (Abstr., 1900, ii, 520, 703) has calculated from the heats of solution, etc., that the heat development of the Clark cell is 81,127 cal. in fair agreement with the value calculated from the variation of the *E.M.F.* with temperature, 81,490 cal. In calculating the latter value, however, an incorrect value of the electrical equivalent of heat has been used. The accurate value of the latter (1 watt-second = 0.2387 cal.) gives 82,402 cal. at 18°, which does not agree with the value calculated from the heats of solution, etc. G. S.

Piezoechemical Studies V. The Transition Element and its Applications. ERNST COHEN, KATSUJI ISOUYE, and C. ECKEN (*Zeitsch. physikal. Chem.*, 1910, 75, 1—29. Compare Abstr., 1909, ii, 981).—The transition temperature $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$ has been determined at intervals of pressure between 1 and 1500 atmospheres by means of so-called transition elements of two types. The first type, a modified Clark cell, was constituted as follows:

| | | |
|---|---|--|
| Electrode reversible with reference to anion. | Saturated solution of zinc sulphate in contact with the stable solid phase of the salt. | Electrode reversible with reference to cation. |
|---|---|--|

The *E.M.F.* of this element under different pressures was measured at temperatures above and below the transition point, and the latter, at a definite pressure, taken as the point at which the curves representing the influence of temperature on the *E.M.F.* above and below the transition temperature intersected. The other arrangement consisted of two cells, one of which contained a saturated solution of zinc sulphate in contact with the stable form of the salt, whilst the solution in the other was in contact with the metastable form of the salt (the hexahydrate). The temperature at which the *E.M.F.* becomes zero when these cells are set in opposition is the transition temperature.

The transition temperatures with the first type of cell are 38.12°, 38.96°, 41.19°, and 42.63°, and with the second type 38.10°, 39.90°, 41.35°, and 42.80° at 1, 500, 1000, and 1500 atmospheres respectively. The result at one atmosphere pressure is only in moderate agreement with those of previous observers, but is fully confirmed by a dilatometer experiment (38.10—38.20°). G. S.

Piezoechemical Studies. VI. ERNST COHEN and KATSUJI ISOUYE (*Zeitsch. physikal. Chem.*, 1910, 75, 219—231. Compare preceding abstract).—The effect of pressure on the *E.M.F.* of the cell of the second type already described (*loc. cit.*) has been determined indirectly by application of the equation: $E_\pi - E_0 = \pi(v_2 - v_1)$, where v_1 and v_2 represent the volumes of the system before and after

the passage of 96,540 coulombs, and π is the pressure. The factor $v_2 - v_1$ has been determined directly by putting pure zinc sulphate heptahydrate in a pycnometer, filling up with toluene as indifferent liquid, and finding the change of volume after transformation to the hexahydrate. Substituting in the above equation, the value $E_{500} - E_0 = 0.00088$ volt is obtained, as compared with the experimental value 0.00108 volt.

Further, the Clausius-Clapeyron equation:

$$dT/dp = 10,333T(\sigma - T)/427.2v,$$

where $(\sigma - T)$ is the change of volume in the transition of zinc sulphate heptahydrate, and v is the accompanying thermal effect, can be employed to find the effect of change of pressure on the transition temperature. Inserting the appropriate values of $(\sigma - T)$ and v , it is found that $dp/dT = 0.0032^\circ$, whereas the experimental value is 0.0036° .

Finally, another equation is derived thermodynamically, by means of which dp/dT can be calculated by means of electrical measurements. It leads to the value of $dp/dT = 0.0027^\circ$, instead of the experimental value given above.

G. S.

Thermo-[electric] Forces of Solid Solutions of Metals and Schenck's Law. AUGUST L. BERNOULLI (*Ann. Physik*, 1910, [iv], 33, 690—706).—Thermo-electric measurements have been made for various solid solutions of metals in order to test Schenck's formula $\pi = R/2e \cdot \log(k' \sigma' : k \sigma)$, in which π is the thermo-electric difference of potential between the pure metal and a solid solution containing a second metal, k and σ are the thermal and electric conductivities of the solvent metal, and k' and σ' the corresponding quantities for the solution.

Solutions of thallium and tin in silver, of mercury in cadmium, and of tin, zinc and nickel in copper, were investigated. For sufficiently dilute solutions the observed thermo-electric potential difference agrees with that calculated from Schenck's formula, and this agreement is particularly good when the atomic weight of the solute metal is considerably greater than that of the solvent metal. As the concentration of the solutions increases, the agreement becomes less satisfactory. In the case of the copper zinc alloys, the observed potential differences are much larger than those obtained by calculation, and this is attributed to the formation of the compound Cu_2Zn_3 .

H. M. D.

Electrophoresis of Lamp Black. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1910, 24, 345—354).—Using an apparatus similar to that described by Coehn (*Abstr.*, 1909, ii, 841), the author has investigated the electrophoresis of lamp black (Kahlbaum's) which had been subjected to different methods of purification in order to obtain a suspension in water. These methods were: (a) treatment with a mixture of potassium dichromate and concentrated sulphuric acid for eighteen hours, and subsequent washing with dilute hydrochloric acid and finally with water; (b) trituration with concentrated sulphuric acid and then washing as in (a); (c) warming with a dilute

solution of sodium in ordinary alcohol, and subsequent washing with alcohol and water; (d) no purification was attempted, but a suspension was obtained directly by introducing the lamp black into dilute alcohol, which was slightly alkaline. Suspensions could not be obtained when it was put directly into water.

The suspensions obtained were investigated as such, and after the addition of enough potassium hydroxide or hydrochloric acid to make them from $N/110$ to $N/11,000$. All alkaline suspensions showed the phenomenon of anaphoresis, and were fairly stable. Suspensions which were very feebly acid still showed anaphoresis, but when the acidity was increased ($N/110$) they were flocculated so rapidly that it was impossible to observe whether they showed cataphoresis (compare Perrin, Abstr., 1905, ii, 138). Details are also given of actual stability of the different suspensions and of the effect of filtration.

The remainder of the paper is occupied with a discussion of the detergent action of soap, special reference being made to the theories of Spring (this vol., i, 6) and of Chevreul. T. S. P.

The Nature of the Coloured Films Formed on the Alkali Metals by Electric Discharges. JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1910, 11, 1082—1083. Compare this vol., ii, 379).

—The coloured substances which are formed on the surface of the alkali metals when subjected to the influence of the glow discharge in hydrogen at low pressure have been described as colloidal solutions of the metals in the corresponding hydrides. It is pointed out that the colours of the different substances are identical with those of the corresponding modifications of the alkali metals obtained by Fischer and Schröter (this vol., ii, 609) by the disintegrating action of the arc discharge on alkali metal electrodes immersed in liquid argon. The two series of coloured substances obtained by the two methods are considered to be identical.

The presence of hydrogen is supposed to facilitate the formation of the colloidal metals under the influence of the glow discharge by forming hydrides which act as solvents for the metals. Since hydrogen was in all probability present in the arc discharge experiments of Fischer and Schröter, the formation of the colloidal metals in these circumstances may be in some measure due to the preliminary formation of hydrides.

When potassium is subjected to the glow discharge at the temperature of liquid air, the coloured film is not formed to any appreciable extent, and this is attributed to the absence of the hydride, which is not formed in consequence of the low vapour pressure of the alkali metal at this temperature. H. M. D.

Specific Heats and Gas Equilibria from Explosion Experiments. II. MATHIAS PIER (*Zeitsch. Elektrochem.*, 1910, 16, 897—903). —The manometer previously used (Abstr., 1909, ii, 789) is improved by fixing the mirror directly to the corrugated diaphragm about midway between its centre and its periphery.

By exploding acetylene (a) with excess of air, (b) with excess of

oxygen, and (c) with excess of carbon dioxide, data are obtained from which the ratios of the specific heats of carbon dioxide or of oxygen to that of nitrogen are calculated. The molecular heat of oxygen, up to 2200° , is the same as that of nitrogen ($4.900 + 0.00045t$). The formulæ of Holborn and of Langen do not represent the results obtained for carbon dioxide; a new equation is therefore proposed for the mean molecular heat of carbon dioxide between 0° and t° at constant volume: $c = 6.800 + 3.3 \times 10^{-3}t - 0.95 \times 10^{-6}t^2 + 0.1 \times 10^{-9}t^3$. This represents both the author's results between 1600° and 2100° and those of Holborn and Henning ($200-1364^{\circ}$), with sufficient accuracy.

The molecular heat of sulphur dioxide is obtained from explosions of carbon disulphide with oxygen. It is the same as that of carbon dioxide up to 2000° .

The dissociation of carbon dioxide is calculated from the results of explosions of mixtures of carbon monoxide and oxygen on the assumptions that carbon monoxide has the same molecular heat as nitrogen, and that the above expression for carbon dioxide holds up to 3000° . The results are too high, which is taken to indicate that the specific heat of carbon dioxide increases more rapidly above 2000° . An attempt to measure the equilibrium $\text{CO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{CO}$ also failed for reasons which are not clearly understood.

T. E.

Critical Phenomena of Ethyl Ether. F. B. YOUNG (*Phil. Mag.*, 1910, 20, 793-828).—Observations relating to the nature of the critical phenomena in ethyl ether are described and discussed in reference to Andrews's theory.

It has been frequently observed that when a liquid in contact with its vapour is heated to the critical temperature, the meniscus disappears, whilst the density of the liquid is still distinctly greater than that of the vapour, and that this difference of density may persist for a considerable time, even when the temperature is raised above the critical temperature. Various explanations of this have been offered, some of which attempt to reconcile it with Andrews's theory, whilst others regard it as evidence of the incompleteness of this theory.

The ethyl ether used in the experiments was purified as completely as possible, and elaborate precautions were taken to free it from traces of air, for observations made with different tubes containing extremely small quantities of gaseous impurities indicate that these may visibly modify the critical phenomena. The Jena glass tubes containing the ether were heated in an aniline vapour-bath, the temperature of which could be adjusted very exactly by regulation of the pressure. Sliding freely inside each tube was a bell-shaped piece of tubing sealed on to a closed tube containing iron filings, which enabled the bell to be raised or lowered by means of an electro-magnet. This arrangement was found to give a very delicate means of testing the contents of the tubes for traces of gaseous impurities.

The conclusion drawn from the observations is that the critical phenomena observed with the pure substance can be explained in accordance with Andrews's theory, and that the phenomena advanced in support of the insufficiency of this theory are to be observed only

in tubes which contain traces of impurities. The part played by hydrostatic pressure is, in all probability, negligibly small, and the differences in density which are observed on the disappearance of the meniscus are apparently due to slight differences in temperature.

From a study of the phenomena of opalescence, the author considers that the opalescence is not due to the formation of an emulsion, but to variations in the temperatures of the individual molecules, as has been supposed by Küster.

In an appendix, a vapour thermostat for experiments on critical phenomena is described. The vapour-jacket is connected with a large flask, which communicates with a closed mercury manometer. This is provided with a short arm, in which is a float which makes electrical contact with a platinum-tipped needle. When contact is made, a relay is actuated, and a current is sent through a coil of fine wire contained in the large flask. The heat developed causes the air to expand until the consequent rise of pressure breaks the contact. By wrapping the coil of wire in cotton wool, the change of pressure is made to take place less suddenly, and the mercury in the gauge is thus enabled to follow the change of pressure more closely.

H. M. D.

Influence of the Surface of a Solid Phase on the Latent Heat and on the Melting Point. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 677—680. Compare *Abstr.*, 1909, ii, 13, 295).

—The formula obtained by the author connecting the melting point with the surface energy of a phase is now deduced by another method, and a further formula is given showing in what direction the melting point of small particles varies as compared with that of large ones. If small particles have a smaller heat of fusion, then the temperature at which they melt is lower than that of the large particles; if their heat of fusion is greater, then the melting point is higher than that of the large ones.

If the free surface energy of a solid phase is less than the free surface energy of the liquid phase, then the increase of surface of the solid phase is accompanied by a rise in its heat of fusion, and vice versa. If the free surface energy of the solid and liquid phases are equal, then the change in the size of the surface exerts no influence on the latent heat of fusion (see further, this vol., ii, 1043).

Z. K.

Influence of Degree of Dispersion of Solid Crystalline Substances on their Melting Points. P. P. VON WEIMARN

(*J. Russ. Phys. Chem. Soc.*, 1910, 42, 647—653).—A short discussion of the author's previous work on this subject. The properties of the surface layer of a crystal resemble, although they are not identical with, those of the interior of a strongly compressed liquid, whilst the superficial layer of a liquid resembles the interior of a strongly compressed gas; therefore, with an increase in the degree of dispersion, a solid, crystalline substance becomes more active chemically, more volatile, more soluble, and more readily fusible. The two most important factors in determining the structure and properties of the surface layer of a crystal are: (1) the unilateral action of the vectorial molecular forces

on the molecules, forming the free surface of the crystal. (*B*) The dynamic (kinetic molecular) processes occurring on the free surface of the crystal. *A* gives rise to the capillary pressure, which is superadded to the external pressure on the surface, and increases with the degree of dispersion; consequently, as the degree of dispersion increases, so *A* tends to diminish the similarity between the surface of the crystal and a liquid, the melting point, in general (except in cases such as ice), rising with an increase in pressure. *B*, on the other hand, tends to increase the similarity between the surface of a crystal and a liquid, and since a fine disperse system is almost always more active than a coarse one, *B* acts as a more energetic factor than *A*. In addition, the melting point is lowered in a system of great dispersion by the fact that the surface of the crystals dissolves the surrounding medium until saturated; consequently, the melting point and other physical properties of a disperse system varies with the nature of the medium by which it is surrounded, or from which the crystals have been separated, and the greater the degree of dispersion the more marked is this variation.

Z. K.

The Spontaneous Crystallisation and the Melting- and Freezing-Point Curves of Mixtures of Two Substances which form Mixed Crystals and Possess a Minimum or Eutectic Freezing Point. Mixtures of Azobenzene and Benzyllaniline. FLORENCE ISAAC (*Proc. Roy. Soc.*, 1910, *A*, 84, 344-369).—From freezing- and melting-point observations with mixtures of azobenzene and benzyllaniline, it has been found that these substances form a eutectic mixture which solidifies at 26° and contains 19% of azobenzene. Mixed crystals are formed by mixtures containing more azobenzene than the eutectic, but not by mixtures which contain less. The form of the melting-point curve was confirmed by analysis of the mixed crystals.

The temperatures at which different mixtures undergo spontaneous crystallisation were also determined by two different methods, and in this way the supersolubility curve was obtained. This curve exhibits a minimum for liquids which have approximately the composition of the eutectic mixture, and, for the most part, it runs nearly parallel to the freezing-point curve. The supersolubility curve, on the other hand, cuts the melting-point curve at three different points. The mixed crystals which separate out on spontaneous crystallisation along the supersolubility curve have been determined for various liquid mixtures of the two substances. Microscopic examination of sections cut from the solid solutions indicates that gradual changes take place in these mixed crystals at the ordinary temperature.

H. M. D.

Freezing Mixtures. JACQUES DECLAUX (*Compt. rend.*, 1910, 151, 715-716).—A description of a simple method for attaining low temperatures. Two liquids, which produce a fall in temperature on mixing, are allowed to flow through two long glass tubes (diameter, 1 mm.). The liquids leave the tubes at the rate of 1 to 2 drops per second, and then mix. The mixture is caused to flow over the tubes before leaving the apparatus, thus lowering the temperature of the incoming liquids. By this method a temperature of -45° can

be maintained for long periods, employing 100 c.c. of carbon disulphide and 70 c.c. of acetone per hour. In one experiment, a volume of 20 c.c. was kept at -43.5° with this mixture in a double-walled, silvered glass tube, the external temperature being 22° . W. O. W.

Condition of Substances in Solution in Absolute Sulphuric Acid. V. GIUSEPPE ODDO and E. SCANDOLA (*Gazzetta*, 1910, 40, ii, 163—209. Compare Abstr., 1909, ii, 377, 792, and Hantzsch, *ibid.*, ii, 973).—Since in the opinion of the authors the condition of alcohols in solution in absolute sulphuric acid has now been settled, they have proceeded to the study of the ethers and esters. In a polemical appendix, the objections raised by Hantzsch are discussed, further inaccuracies in his results are suggested, and finally the authors' views on the whole question under examination are set forth.

In calculating from the cryoscopic measurements the molecular weights of the substances in solution, a correction is introduced for the proportion of the dissolved substance which has been acted on by the sulphuric acid, the correction being obtained by neutralising the remaining sulphuric acid with barium hydroxide and weighing the barium sulphate obtained. When this is done, it is found that the molecular weights amount to very nearly 50% of the theoretical in the case of all the following ethers: ethyl ether, propyl ether, *n*-butyl ether, *iso*amyl ether, *n*-heptyl ether, dimethylpyrone. Hence all these ethers yield an acid oxonium sulphate which dissociates.

In the case of the esters ethyl acetate and ethyl monochloroacetate, it is found that decomposition (to the extent of 15.35% and 32.9%, respectively) occurs, although Hantzsch has stated otherwise in regard to the former substance. Taking this decomposition into account, the molecular weights are 55% and 62% respectively of the theoretical values, showing that the esters are weaker oxonium bases than the ethers, the weakness being greater the more negative the radicle which they contain. The authors consider that when an ester is dissolved in absolute sulphuric acid, three changes occur: (1) formation of the acid oxonium sulphate, which dissociates into two ions; (2) molecular dissociation of part of this salt; (3) partial decomposition of the ester into two acids, namely, the alkyl hydrogen sulphate, and the acid corresponding with the contained radicle. Of these, the second tends to give values above 50%, the third values below that. Hence the mere cryoscopic measurement may indicate 50%. Results according with this view were obtained also with *iso*amyl formate, *iso*amyl acetate, and *iso*amyl butyrate.

Experiments with ethyl nitrate, *iso*amyl nitrate, and *iso*amyl nitrite show that with increase in the negative character of the acid radicle (as compared with those of the ethers and esters already mentioned), the acid decomposition of the molecules reaches a maximum, and no indication of an oxonium salt can be found. *sec*-Butyl nitrate gives results indicating that the difference between primary and secondary alcohols already noticed (*loc. cit.*) exists also in the case of the esters. Methyl sulphate has not the normal molecular weight, as stated by Hantzsch. On the contrary, the authors advance reasons for supposing that a large part of it is decomposed to form the

acid ester, and that in addition complex molecules, such as $\text{Me}_2(\text{HSO}_4)_2$, also exist in the solution.

R. V. S.

Some Molecular Weights in Phosphoryl Chloride as a Cryoscopic Solvent. PAUL WALDEN (*Zeitsch. anorg. Chem.*, 1910, 68, 307—316).—Phosphoryl chloride has been used as a cryoscopic solvent by Oddo (Abstr., 1901, ii, 492,; 1904, ii, 236), who found the melting point to be -1.782° , and the cryoscopic constant 70.16 . The author finds the melting point to be $+1.25^\circ$, and the cryoscopic constant, determined as the mean of experiments with several compounds, 76.8 , corresponding with a latent heat of fusion of 19.8 Cal.

Simple molecular weights are given by the compounds ICl , IOX , N_2O_3 , Cl_2O_7 , and OsO_4 . Phosphoric oxide, chromic acid, and iodine pentoxide are practically insoluble in phosphoryl chloride.

The cryoscopic constant of bromoform is 144 . Both solid α - and liquid β -iodine chloride are unimolecular in bromoform.

C. H. D.

Dicyclohexyl as a Cryoscopic Solvent. LUIGI MASCARELLI and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 410—414).—For the purpose of comparison with cyclohexane (Abstr., 1909, ii, 19, 972) the behaviour of dicyclohexyl, $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_{11}$, prepared by the reduction of diphenyl by hydrogen in the presence of nickel, has been examined. The cryoscopic constant has a mean value of 145.2 . The solubility of most substances in this solvent in the cold is small. Phenol, propyl alcohol, and acetic acid are associated, even in dilute solution. The general behaviour of ketones and nitro-compounds in dicyclohexyl closely resembles that of the same substances in cyclohexane. Tetranitromethane, however, is normal.

C. H. D.

Vapour Pressure Curves. DEMETRIUS E. TSAKALOTOS (*Zeitsch. physikal. Chem.*, 1910, 75, 743—746. Compare this vol., ii, 266).—The minimum of vapour pressure in the binary mixture chloroform-ethyl ether is probably connected with the formation of a compound $\text{Et}_2\text{O}\cdot\text{CHCl}_3$. From the results of surface-tension and vapour pressure measurements, it appears that liquid oxygen is polymerised, whereas according to Walden's boiling-point formula (Abstr., 1909, ii, 122) it is unimolecular.

G. S.

Studies in Vapour Pressure. III. A Static Method for Determining the Vapour Pressures of Solids and Liquids. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, 32, 1412—1434; *Ann. Physik*, 1910, [iv], 33, 971—978. Compare this vol., ii, 687, 688).—The sources of error involved in vapour pressure measurements are discussed, and a critical résumé is given of the various methods which have been employed in such determinations. A new form of apparatus, called the *static isothermoscope*, is described, and it is claimed that by means of this apparatus more trustworthy measurements of vapour pressures can be made than by the older methods. It consists of a small U-tube, one limb of which is connected with a small spherical bulb, and the other with a long vertical tube, which communicates with a mercury

gauge and with a large iron bottle, which in turn can be put into communication with (1) the atmosphere, (2) a vacuum reservoir and water pump, or (3) a pressure reservoir and compression pump. The lower half of the U-tube is occupied by a confining liquid, and to prevent the ascent of this into the spherical bulb containing the vaporising liquid or into the long vertical tube, small bulbs are blown on the upper end of each limb of the U-tube. The liquid under investigation may be conveniently employed as confining liquid.

In the manipulation of the apparatus, the temperature of the liquid bath, in which the isoteniscope is immersed, is fixed, and the pressure in the iron bottle is then adjusted until the liquid in the bulb boils freely. After the removal of all air and dissolved gases, the pressure is cautiously increased until the levels of the confining liquid are the same in both limbs of the U-tube. To ensure that all foreign gases have been expelled, the process of boiling and adjusting of the pressure is repeated until constant pressure values are recorded on the gauge.

To test the results obtainable with this apparatus, the authors have measured the vapour pressure of water between 50° and 90°, the isoteniscope being immersed in a thermostat, the temperature of which was determined by means of a resistance thermometer. The data obtained are in close agreement with the measurements of Holborn and Henning.

H. M. D.

Studies in Vapour Pressure. IV. A Redetermination of the Vapour Pressures of Mercury from 250° to 435°. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, 32, 1434—1447; *Ann. Physik*, 1910, [iv], 33, 979—988).—The measurements were made by means of the static isoteniscope (compare preceding abstract). From the vapour pressures, 106.52 mm. at 264.16°, 760 mm. at 356.95°, and 2598.67 mm. at 433.96°, a Kirchhoff-Rankine-Dupré formula has been obtained, which may be written: $\log p = 9.9073436 - 3276.628/\theta - 0.6519904 \log \theta$. The experimental data, which agree well with the pressures calculated from this equation, are compared with the older measurements of Gebhardt, Regnault, Ramsay and Young, and with the probable values calculated by Laby (*Abstr.*, 1908, ii, 1039) from the several known series. The divergences between the authors' measurements and the values adopted by Laby are not inconsiderable, the difference amounting to 15 mm. at 450°.

A table is given showing the vapour pressures of mercury for every 2° between 0° and 450°; these pressures are the values obtained from the formula given above. The temperatures refer to the thermodynamic scale, and the pressures to the normal value of gravity.

H. M. D.

Studies in Vapour Pressure. V. A Dynamic Method for Measuring Vapour Pressures, with its Application to Benzene and Ammonium Chloride. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, 32, 1448—1459; *Ann. Physik*, 1910, [iv], 33, 989—994).—The authors describe a modified form of

apparatus for the dynamic measurement of vapour pressures (compare this vol., ii, 687, 688). The apparatus, which is immersed in a well-stirred liquid bath, consists of a small bulb, which communicates through a narrow tube with a small reservoir containing a suitable confining liquid. The tube is sealed through the upper wall of the reservoir, and terminates beneath the surface of the confining liquid. By means of a long vertical tube, the reservoir can be put into communication with a pump or compression apparatus.

This so-called *dynamic isotenoscope* has been employed for the measurement of the vapour pressure of benzene between 65° and 120°, and that of ammonium chloride between 280° and 333.5°. The results are compared with those of previous observers, who have used both static and dynamic methods of measurement. In the case of ammonium chloride, the authors' vapour pressure curve lies between the curves representing the data of Ramsay and Young and those of Johnson (Abstr., 1908, ii, 157).
H. M. D.

The Composition and Vapour Tension of Solutions. III. The Influence of Temperature on the Composition of Solutions. M. S. VREYSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 702—714).—The solutions of ethyl, methyl, and propyl alcohol in water have been investigated. Curves are given showing the relation between the %molecular composition of the solutions and the %molecular composition of the vapour at various temperatures for each pair of liquids, and the composition of the constant boiling point solution of propyl alcohol and water is deduced graphically. As the temperature of the solution of methyl and ethyl alcohol in water rises, the relative proportion of water in the vapour increases, whilst in the case of propyl alcohol, the proportion of alcohol in the vapour increases under similar conditions. These facts are deduced theoretically and shown to agree with experiment.
Z. K.

Micro-distilling Apparatus. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1910, 49, 744—745).—The apparatus consists of a very small flask (or test-tube), the neck of which is shaped like the head of an alembic. For very volatile liquids, by means of a cork, a small, inverted condenser is attached, the tube from which is bent slightly so that the liquid which drops from it will fall into the annular space in the alembic head.
L. DE K.

Measurement of Heats of Combustion with the Calorimetric Bomb and Platinum Resistance Thermometer. FRANZ WAGNE (*Zeitsch. physikal. Chem.*, 1910, 75, 81—94).—A number of other determinations of heats of combustion has been made by the method already described (Abstr., 1908, ii, 155). The heats of combustion in joules per gram are as follows: phenylacetic acid, 28.618; α -methyl glucoside, 18.175; naphthalene, 40.314; furoin, 23.941; glycine, 13.035; *DL*-alanine, 18.218; *D*-alanine, 18.217; *DL*-valine, 25.045; glycine anhydride, 17.441; *D*-alanine anhydride, 23.163; *DL*-leucyl-glycine, 24.367; formyl-*DL*-leucine, 24.134; diglycylglycine, 15.732; triglycylglycine, 16.119; glycylglycinecarboxylic acid, 11.234; methyl-uracil, 18.688; and isoserine, 13.709.

The sources of error in the work of previous observers, and the possibility of applying corrections to their data are discussed.

G. S.

Solutions. II. Variation of Density of Binary Mixtures with Temperature. F. SCHWERS (*Bull. Soc. chim.*, 1910, [iv], 7, 937—940).—In previous papers (Abstr., 1909, i, 80, ii, 794) it has been shown that if changes of volume are expressed in percentages of the initial volume, the volume-temperature curve for a binary liquid mixture is sinuous and shows characteristic inflexions. It can be superposed on that illustrating the relationship between refractive index and temperature for the same mixture (this vol., ii, 913), and is similar in form to the curve expressing the relationship between heat developed and temperature of admixture, for the same mixture. These observations cannot be explained by the hydrate theory of solutions, and the following explanation is suggested. Admixture of two liquids may cause disintegration of associated molecules, the existence of which was proved by Ramsay and Shields (*Trans.*, 1893, 63, 1089). Such disintegration causes, according to van Laar (Abstr., 1900, ii, 189), a diminution in volume. In a mixture this may be counterbalanced in part, or overbalanced, by an increase in volume due to a new association between different molecules. In raising the temperature of such a system, each complex formed will undergo disintegration in accordance with its own constant of dissociation, and since this constant is not a linear function for a single liquid, it is conceivable that such changes occurring in a mixed system may be represented by a sinuous curve.

T. A. H.

New Theory of Molecular Volumes. GERVAISE LE BAS (*Chem. News*, 1910, 102, 226—229).—The volumes of a number of atoms or groups in straight chain compounds or in the side chains of ring compounds have been calculated as described in previous papers compare Abstr., 1907, ii, 754; 1908, ii, 667). The results are as follows: OH = 11.1 = 3H; CO·OH = 37.0 = 10H; CO₂ = 33.3 = 9H; NO = 22.2 = 6H (except in CO·OH group, where CO = 25.9 = 7H); HO = 25.9 = 7H. Oxygen in the hydroxyl group generally, in the phenolic ethers, and in aldehydes and ketones = 2H; in the carbonyl group and in the aliphatic ethers it is equal to 3H. Doubly linked oxygen in a ring is also equal to 3H.

The volumes of a number of ring compounds containing oxygen are tabulated, and it is shown that ring structure is accompanied by considerable contraction, which varies in magnitude with the size and complexity of the ring. The relative volumes are, however, the same in spite of the contraction.

G. S.

Method for Determining the Lower and Upper Limits of Elasticity. The Hardening of Metals. O. PAUST and GUSTAV FARMANN (*Zeitsch. physikal. Chem.*, 1910, 75, 108—126).—The lower limit of elasticity of a metal can be determined by subjecting a piece of which one side is highly polished to pressure or to a pull, and observing microscopically the point at which the polish just begins to disappear. The elasticity can be increased by alternately slowly

increasing the pressure beyond the first limit of elasticity, and then releasing, until finally an upper limit of elasticity, corresponding with the limiting pressure which produces flow in the metal, is reached. The metal has, therefore, been hardened by slowly increasing the pressure. Some of the data for the lower and upper limits of elasticity are as follows: lead, lower limit 25 kilog./cm.², upper limit 102 kilog. cm.²; zinc, drawn, lower limit 75, upper limit 770 kilog./cm.²; copper, drawn, lower limit 1200, upper limit 2780 kilog./cm.². The lower limit depends greatly on the previous treatment of the sample.

* The hardening of metals is ascribed, not to formation of a harder crystalline form, or to a change to the amorphous condition, but to a diminution in the size of the crystallites of which the metal is composed, owing to the formation of systems of sliding surfaces. The hardening is, therefore, a preparation for flowing, the latter occurring when the systems of sliding surfaces have sufficiently increased. Detailed evidence in favour of this view of hardening is advanced.

G. S.

Viscosity of Isodynamic and Motoisomerides. FERDINAND B. THOLE (*Zeitsch. physikal. Chem.*, 1910, 74, 683—686).—Mühlenthein (*Dissertation*, Cöthen, 1907) has found that the densities and viscosities of nitrobenzene and of quinoline altered on keeping, and ascribed this result to the existence of these compounds in two isomeric forms. The author has prepared pure specimens of these compounds, and finds no difference in the viscosities or densities immediately after distillation, and after twenty-two hours. For nitrobenzene, D_4^{25} 1.1987, viscosity at 25° = 0.018224; for quinoline, D_4^{25} 1.08994, viscosity = 0.033724.

The statement of Schaum (*Abstr.*, 1898, i, 629) that the density of ethyl acetoacetate alters when kept is confirmed; the viscosity alters in a corresponding manner. The viscosity of the diethyl derivative of this ester, which cannot have an enolic constitution, and of ethyl malonate did not alter on keeping.

G. S.

Viscosity of Albumin Solutions. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1910, 23, 353—354).—Polemical against Pauli and Wagner (this vol., ii, 830). The author maintains the validity of his measurements of the isoelectric point.

G. S.

Influence of Chemical Affinity in Certain Adsorption Phenomena. LÉO VIGON (*Compt. rend.*, 1910, 151, 673—675; *Bull. Soc. chim.*, 1910, [iv], 7, 985—988. Compare this vol., ii, 273, 275, 692).—The phenomena of adsorption may be divided into two classes: those due to attraction between chemically inert substances in colloidal solution or in suspension, and those due to chemical affinity between two substances, one of which is insoluble whilst the other is in true solution, or between two insoluble substances having some degree of chemical activity. Thus inert compounds, like calcined silica or asbestos, have no attraction for picric acid in aqueous solution, whilst in the case of zinc oxide or aluminium hydroxide the acid is adsorbed. Quartz adsorbs the alkali hydroxides or carbonates, but not the

chlorides of sodium or magnesium. Brigg's results (Abstr., 1906, ii, 13) are discussed from this point of view. W. O. W.

Adsorption of Gases by Charcoal. ALEXANDER TITOFF (*Zeitsch. physikal. Chem.*, 1910, 74, 641—678. Compare Homfray, this vol., ii, 771).—The adsorption of hydrogen, nitrogen, carbon dioxide, and ammonia by coconut charcoal has been measured between -79° and $+151.5^{\circ}$ by the usual method. Between -80° and $+80^{\circ}$ the adsorption of hydrogen follows Henry's law, while the behaviour of the other gases at constant temperature is represented by the familiar formula $a_t = ap_t^{1/n}$, where a_t represents the amount of gas adsorbed at the pressure p_t , and a and $1/n$ are constants. When both pressure and temperature are varied, the results are represented by the formula $\log a_t = \log a_0 - (x - y \log p)/t$, where x and y are constants bearing a simple relationship to a and $1/n$. Deviations from these formulæ occur in the cases of carbon dioxide and ammonia at the higher pressures, under which conditions the gases are probably partly liquefied. Ammonia was adsorbed to the greatest extent; at 0° and 10 cm. pressure, 1 gram of charcoal adsorbed 71 c.c. of this gas.

The heats of adsorption, q , of nitrogen, carbon dioxide, and ammonia gases were determined by means of an ice calorimeter. The mean values of q at 0° for 1 c.c. of gas are as follows: nitrogen 0.203 cal., carbon dioxide 0.31 cal., and ammonia 0.386 cal., each about 50 cm. pressure, the results for the last two gases being in good agreement with those obtained by Chappius (Abstr., 1883, 702). The values of q diminish considerably with increasing pressure. The heats of absorption have also been calculated from the isothermal adsorption curves by means of the formula $-q = nRT^2(x \times y \log p)/22.4 \log e$, and there is fair agreement between the calculated and experimental values. G. S.

Absorption of Gases by Charcoal. IDA F. HOMFRAY (*Zeitsch. physikal. Chem.*, 1910, 74, 687—688. Compare this vol., ii, 771).—A few slight corrections to the former paper (*loc. cit.*) and some additional references are given. G. S.

Adsorption of Solutions [by Charcoal]. GERHARD C. SCHMIDT (*Zeitsch. physikal. Chem.*, 1910, 74, 689—737. Compare Abstr., 1895, ii, 39).—In the great majority of the experiments the adsorption of acetic acid from aqueous solution was studied. The rapidity with which equilibrium is established depends on the nature of the charcoal; with some specimens it is practically instantaneous at room temperature. At low temperatures, the equilibrium is reached very slowly; increase of temperature enormously accelerates the adsorption. This is due, at least in part, to the more rapid removal of gases adsorbed (chiefly air) in the fine pores of the material as the temperature is raised. When equilibrium is attained, and the solution then diluted, the new equilibrium point is rapidly reached, the rate being the greater the more the concentration is altered. If, on the other hand, a more concentrated solution is added to a system already in equilibrium, the new equilibrium point is only slowly attained.

It is shown by experiments with acetic acid in aqueous solution

that on gradually increasing the concentration a maximum of adsorption is reached, a fact which shows that the usual adsorption formulæ cannot be valid within wide limits. A new formula, $\log[S/(S-x)] - Ax = C(a/v)$, is derived, S representing the maximum of adsorption, x the amount adsorbed, a the total amount of the solute, v the volume, and A and C are constants depending on the amount and nature of the coal. This formula represents the experimental results fairly satisfactorily. There are, therefore, three determining factors in adsorption: S , the maximum adsorption, K (proportional to C), the activity coefficient of the material, and A , which is a measure of the falling off in the attraction between adsorbing surface and solute as the amount adsorbed increases.

From experiments with iodine and acetic acid in chloroform solution it is shown that the amount of two dissolved substances adsorbed from a solution containing both is less than the sum of the amounts adsorbed separately. Further, when charcoal is in equilibrium with one solute, and a second is added, it partially displaces the first substance from combination.

Some experiments on the adsorption of acetic acid from solution in ethyl acetate are described. G. S.

Dissociation of Ferric Sulphate. MAX BODENSTEIN and TATSUO SUZUKI (*Zeitsch. Elektrochem.*, 1910, 16, 912—916).—The measurements of Wöhler, Plüddemann, and Wöhler (Abstr., 1908, ii, 290) of the partial pressure of sulphur trioxide in equilibrium with ferric sulphate gave values three or more times larger than those of Keppeler and D'Aus (Abstr., 1908, ii, 289). The authors have therefore repeated both sets of experiments, taking every precaution to avoid accidental errors, and have obtained results which agree very well with the original measurements in both cases. In Wöhler's method the total pressure of the mixture of sulphur di- and tri-oxide and oxygen evolved by the heated ferric sulphate is measured, and the partial pressure of the trioxide calculated from Bodenstein and Pohl's measurements of the equilibrium constant. It is shown that the gases really are in equilibrium, and that this method of calculation is therefore justified. On the other hand, in Keppeler's method of passing air or nitrogen over the heated ferric sulphate, although the partial pressure of trioxide found is independent of the velocity of the gas within the rather narrow limits tried, the ratio between the oxides of sulphur and the oxygen is not in agreement with Bodenstein and Pohl's measurements of the dissociation of sulphur trioxide; there is always too little trioxide. The deviation diminishes as the temperature rises. It appears therefore that the low results obtained in Keppeler's experiments are due to equilibrium not being established. If ferric sulphate dissociates directly into ferric oxide and sulphur trioxide, an excess of trioxide would be anticipated instead of a deficit, hence the mechanism of the reaction is probably more complicated. T. E.

The Theory of Transpiration, Diffusion, and Thermal Conduction in Rarefied Gases. MARYAN SMOLUCHOWSKI (*Bull. Acad. Sci. Cracow*, 1910, 7A, 295—312).—The paper consists of three

sections. The first and second are concerned with a criticism of Knudsen's recent papers on the dynamics of rarefied gases (Abstr. 1909, ii, 216; *Ann. Physik*, 1910, 31, 205, 633) from the theoretical standpoint. It is stated that the treatment of the problems is invalidated by the neglect to take into account the modification of the Maxwell-Boltzmann law of distribution of velocities during thermal conductivity and diffusion. An expression is deduced for the increase of thermal conductivity of gases produced by molecular surface currents. An analysis for the condition of low pressure, where the mean free path of the molecule is large compared with the dimension of the vessel, leads to results somewhat similar to those of Knudsen, but, it is claimed, by a simpler and more rigorous method. The last section contains a discussion of the experimental results of Soddy and Berry on the conduction of heat through rarefied gases (this vol. ii, 180). An exact calculation of the theoretical conduction of heat gives as the result that their values should be multiplied by the factor $\sqrt{\pi/6} = 0.7236$, and by the term $1 - \beta + \beta$, where β is a coefficient representing the fraction of the total number of molecules "reflected" from the surface without change of kinetic energy. A recalculation of their results shows that β can never be neglected, the interchange of energy between the surface and the molecule impinging upon it being the less perfect the lighter the molecule and the greater its intramolecular energy. F. S.

Methods of Investigation of Capillary-chemical Problems. P. N. Fawcett (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 265—267).—From a consideration of surface-energy relationships, von Weimarn arrived at the conclusion that a substance in a very fine state of subdivision should melt at a higher temperature than that found for the substance in the form of coarse particles. Since this conclusion is contradicted by experiment, some doubt has been thrown on the validity of the deductions made on the basis of surface-energy considerations. The author points out that the conditions under which a melting-point determination is carried out in the ordinary way preclude the possibility of observing the effect which is to be expected on the basis of Laplace's theory of capillarity.

von Weimarn's views relative to the nature of the surface layer of crystalline substances are also criticised. The assumption that the properties of the surface layer approximate to those of the inner layers of a highly compressed liquid is tantamount to the view that the surface layer is isotropic, whereas the geometric and physical characteristics of crystalline substances indicate that the surface layer is anisotropic (compare this vol. ii, 1033). H. M. D.

Osmotic Equilibrium between Two Fluid Phases. L. GAY (*Compt. rend.*, 1910, 151, 754—756. Compare this vol. ii, 935).—The mathematical considerations advanced in a previous paper lead to the proposition that for two fluid phases in osmotic equilibrium with a common constituent at infinite dilution, at the same temperature and pressure, the variations in volume and thermal effects should be equal.

whatever the temperature and pressure. Some theoretical consequences of this conclusion are discussed in the present communication.

W. O. W.

Diffusion [of Dissolved Substances]. OSCARRE SCARPA (*Novo Cimento*, 1910, [v], 20, 212—225).—Vanzetti (Abstr., 1908, ii, 29, 88; 1909, ii, 978) has compared the coefficient of diffusion of certain electrolytes by allowing them to diffuse towards each other in a capillary tube filled with distilled water, and finding (for example, with silver nitrate and alkali chlorides) where a precipitate begins to appear. The author has deduced an equation which permits of the calculation of the coefficient of diffusion of one of the electrolytes in terms of that of the other, of the concentrations of the two electrolytes, and of the position in the tube where the precipitate begins to form.

It is shown that some of the assumptions of Vanzetti, for example, that the distances traversed by the salts are proportional to the coefficients of diffusion, are untenable. The values of the diffusion coefficients obtained by the above method agree neither with the theoretical values nor with those determined by the standard methods; the method is therefore not adapted to the study of diffusion.

The suggestion of Vanzetti that certain of his results are due to the hydrolysis of sodium chloride and other salts in very dilute solution is shown to be untenable. An equation is given which permits of the calculation of the hydrolysis of a salt of a strong base and a strong acid, and it is shown that the degree of hydrolysis is almost independent of the dilution, and therefore the quantity of salt hydrolysed diminishes with dilution, whereas Vanzetti has assumed that it increases.

G. S.

Fundamental Law for a General Theory of Solutions.

EDWARD W. WASHBURN (*J. Chim. Phys.*, 1910, 8, 538—568. Compare this vol., ii, 391).—The interdependence of the colligative properties of solutions (osmotic pressure, b. p., f. p., vapour pressure, etc.) follows from the laws of thermodynamics, and has no bearing on the question of the actual condition of solvent and solute. An ideal solution is one in which neither association nor dissociation of the solute nor association of solute with solvent (solvation) occur. In dilute solutions the molecular concentration of the solute is unaffected by solvation, so that dilute solutions of substances which neither associate nor dissociate behave as ideal solutions. The author develops the following general equation of state for solutions, which, whilst closely related to that advocated by van Laar, is expressed in terms of colligative properties rather than thermodynamic potentials: $d\pi = (-RT/V)\log N$, where π is the osmotic pressure, V the molecular volume, and N the molecular concentration of the solvent.

Physical properties in ideal solutions or mixtures are additive. The vapour tension of any volatile component, such as the solvent $p = p_0 N$, where p_0 is the tension of the pure component. This rule is known to hold in the case of many mixtures of analogous organic substances, such as were examined by Young (Trans., 1903, 83, 68).

Somewhat complex expressions are deduced for freezing point, boiling point, and the effects of concentration and temperature on chemical equilibrium in ideal solutions.

These laws of ideal solution apply to dilute solutions and to certain liquid mixtures, but in most concentrated solutions they are set aside by the unknown factors of association, and dissociation. R. J. C.

A Simple Method of Measuring the Affinity between the solvent and the Dissolved Substance. P. P. VON WEIMARN *J. Russ. Phys. Chem. Soc.*, 1910, 42, 646—647).—If a solvent Y contains in solution the substances $X_1, X_2, X_3, \dots, X_k$, the solutions being of considerable and equal concentrations, and another solvent Z , completely miscible with Y , but practically not dissolving $X_1, X_2, X_3, \dots, X_k$, be added, these substances will be precipitated when sufficient of Z has been added, and the more affinity the dissolved substance bears to Y the more of Z will be necessary. Thus the quantity of Z necessary to completely precipitate X_1, X_2, \dots, X_k from unit value of Y solution will be a measure of the affinity X_1, X_2, \dots, X_k bears to Y . The method has been applied to the solutions of various salts, etc. Z. K.

Partition Law in Mixed Solvents. II. WALTER HERZ and ALFRED KURZER (*Zeitsch. Elektrochem.*, 1910, 16, 869—872).—In addition to the cases previously studied (this vol., ii, 399), the partition of boric acid between water and mixtures of amyl alcohol and carbon disulphide, of iodine between chloroform and mixtures of water and glycerol, of bromine between water and mixtures of carbon tetrachloride and carbon disulphide are investigated. The partition constants for mixtures of two solvents usually differ from the values calculated from the constants of the pure constituents in the sense that the solute is less soluble in the mixture. Two more complicated cases (the partition of picric acid between water and mixtures of chloroform and toluene, and that of iodine between a solution of ammonium iodide and mixtures of carbon disulphide and carbon tetrachloride) are also examined, and found to follow the same laws which hold for single solvents. The results in the second case indicate the existence of BaI_4 molecules in the aqueous solution. T. E.

Diminution of Velocity of Crystallisation by Addition of Foreign Substances. HERBERT FREUNDLICH (*Zeitsch. physikal. Chem.*, 1910, 75, 245—256).—On the basis of the experimental data of von Beckardt (*Abstr.*, 1903, ii, 66) and of Padoa and Galeati (*Abstr.*, 1904, i, 714), it is shown that the diminution in the maximum velocity of crystallisation of supercooled liquids due to the addition of foreign substances is represented by the formula $G_0 - G = kc^{1/n}$, where G_0 is the velocity of crystallisation of the fused solvent, G that of the solution, c is the concentration, and k and n are constants; $1/n$ usually lies between 0.2 and 0.7. This can be accounted for on the assumption that the solvent is adsorbed at the crystal faces, and that the diminution in the velocity of crystallisation is proportional to the amount adsorbed (compare Mare, *Abstr.*, 1909, ii, 983). G. S.

Crystallisation of Agar-agar and Gelatin in Connection with the Mechanism of Gelatinisation. P. P. VON WEIMANN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 653—657).—The author rejects the generally accepted theory that solutions of gelatin, agar-agar, albumin, or other high molecular compounds are disperse systems, liquid α liquid, which are termed emulsoids, and that the gelatinisation of these systems is merely a separation of the two liquids into layers. The solution of such high molecular substances must, on the contrary, be regarded as true solutions, and their gelatinisation as being identical with the process of crystallisation. To obtain emulsoids and suspensoids, a solid substance X is dissolved in a solvent A , and another solvent B , which is miscible in all proportions with A , but does not dissolve X , is added. If the solution is concentrated, the addition of B will at first cause the formation of an emulsion, which will rapidly separate into two layers, X soon crystallising from the layer of A containing it. If a large volume of B is added and the mixture stirred vigorously, X may separate at once. If, however, a fairly dilute solution of X in A is taken, then the addition of B will produce a more stable emulsion and emulsoid, which will only crystallise after very long standing, and the crystals may be microscopic, ultramicroscopic, or even smaller, whilst if the solution is very dilute, the addition of B will at once produce a stable suspension and suspensoid. These considerations have been verified by experiments with manganese sulphate, lithium chromate, potassium carbonate, hydrogen carbonate, and formate, A being water, B an alcohol. With slight modifications, similar experiments with agar-agar and gelatin gave the same results. To obtain a partial precipitation of agar-agar and gelatin the suspensoid was alternately boiled and cooled, alcohol being added to replace that lost by evaporation. The precipitate thus obtained consisted of very minute, long, crystalline grains rounded at the edges.
Z. K.

Behaviour of Salts of Organic Acids on Melting. DANIEL VORLANDER (*Ber.*, 1910, 43, 3120—3135).—In previous papers (*Abstr.*, 1906, i, 317; 1907, ii, 70, 337, 441, 412; 1908, i, 641; ii, 22, 83) attention has been directed to the connexion between the chemical constitution of substances and their power of forming liquid crystals, and in the present paper this investigation is extended, and it is shown that liquid crystals are formed by salts of aliphatic and aromatic acids and by metallic derivatives of phenols, but not by aliphatic hydrocarbons, acids, esters, alcohols, or ketones.

The liquid crystals belong to the same system as those described previously (*Abstr.*, 1908, ii, 88). The salts of the optically active acids are not pleochroic, but certain of them show a play of colours in the liquid crystal state (compare *Abstr.*, 1908, i, 611). The formation of liquid crystals is shown to depend on polarity of structure in the molecule, and their stability and capacity for growing in the direction of the principal axis is due mainly to intramolecular energy difference.

[With R. WILKE and M. E. HUTT.]—The sodium and potassium salts of the normal fatty acids from acetic to cerotic were examined.

and it was found that the property of forming liquid crystals begins with butyric acid and ends with stearic, cerotic acid forming "resinous crystals" in the case of the sodium salt, and doubtful "resinous crystals" in that of the potassium salt. A large number of salts with other metals, particularly for the lower acids, were also examined, and details of the behaviour of these on melting are given. Tetramethylammonium stearate forms a liquid crystal phase.

Sodium allylacetate is a good material for the demonstration of liquid crystals, and the sodium salts of undecylenic, elaidic, erucic, and other unsaturated acids also show this phenomenon.

[With M. E. HURN.]—The tendency to form liquid crystals is greatly influenced by the branching of the chain of carbon atoms, at least among the sodium salts of fatty acids; thus *isovaleric* and *isopropylacetic* acids yield sodium salts, which form liquid crystals, whilst *2-methylbutyric* and *di-2-methylpropionic* acids do not, but the potassium salts of all four show this phenomenon.

The alkali salts of the di- and tri-basic fatty acids do not give liquid crystals as a rule.

The alkali salts of the aromatic acids in many cases yield liquid crystals, but no general correlation with constitution can be deduced. Among substituted benzoic acids the salts of *ortho*-, *meta*-, and *para*-derivatives show equal facility in giving liquid crystals, but the *ortho*-compounds are usually *monotropic*, whilst the *isomeric meta*- and *para*-substances are *enantiotropic*.

Among phenols, only the potassium derivatives of *o*- and *p*-nitrophenol show the phenomenon.

In carrying out these investigations, great difficulty is experienced in observing the two melting points, and the use of the polarisation microscope with crossed Nicols is unadvisable, owing to the difficulty of observing the temperature. For substances of high melting point, Linne's heating apparatus, as constructed by Fuess, is used, and for substances of low melting point, a small melting tube with a stirrer of capillary glass tube or a platinum wire. Approximate first and second melting points for a long series of salts of organic acids, thus determined, are given in the original.

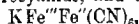
T. A. H.

Proof of the Movements of Dissolved Molecules Demanded by the Molecular Kinetic Theory. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1910, 74, 738—742).—In a previous paper (compare *ibid.*, vol. ii, 772) it has been shown that the movements of particles in a colloidal solution is such that the mean deviation from the average number of particles in a definite volume of solution corresponds with that required by the kinetic theory. The same is now proved to be the case for dissolved molecules as a result of experiments with a solution of polonium chloride. A small portion of the solution was covered with a screen coated with zinc sulphide, and the number of α -particles produced in a given time numbered by observing the impacts on the screen in the usual way. When allowance is made for the deviation from the mean owing to the irregular breaking-down of the radioactive atoms, it is found that the momentary differences of

concentration in a limited volume of a true solution correspond with the requirements of the molecular-kinetic theory. G. S.

[History of the Orientation Theory of Matter.] P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 256—265).—A historical account is given of the views which have been put forward at different times in reference to the nature of the "amorphous" state. Quotations are given from papers by Fuchs, Frankenheim, and Lehmann. H. M. D.

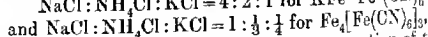
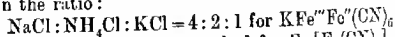
Coagulation of Colloids. V. A. VOLSCHIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 863—876).—The non-agreement between the numbers obtained by various authors for the coagulating power of the same and analogous coagulating substances is probably due to the various methods employed for obtaining colloidal solutions, the different methods of experiment, and to the varying concentrations of the colloid investigated. To characterise the coagulating power of an ion by a number, it is necessary to investigate: (1) the connexion between the concentration of the coagulating ion and the concentration of the colloid precipitated. (2) Whether this relation is identical or not for ions of different valencies. (3) Whether this relation remains the same for different colloids. The present paper is the first of a series to determine these questions. Soluble Prussian-blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, as obtained directly by the interaction of ferric chloride and potassium ferrocyanide, and the insoluble blue,



in oxalic acid solution were used as colloids, and sodium, potassium and ammonium chlorides as coagulating electrolytes. The main portion of the latter was added from a burette to the colloid of given concentration, and the rest added in very small portions or drop by drop, a small portion of the mixture being withdrawn by a capillary pipette and examined under the microscope after each addition. The commencement of the coagulation could thus be accurately determined. Tables and curves are given showing the number of gram-mols. and concentration of electrolyte necessary to coagulate colloid solution of varying concentration.

The curve for each electrolyte is of exactly the same character, resembling the crystallisation curves in a mixture of two salts. It consists in each case of branches, the breaks coming at exactly the same points on the abscissæ (where are marked the total volume of colloid + electrolyte at coagulation point).

The ordinates (gram-mols. of electrolyte) corresponding with these points are in the ratio:



and these relations are true whatever the concentration of the colloid. Coagulation by means of electrolytes, although in some respects a purely physical phenomena, may yet exhibit laws characteristic of purely chemical processes, and this is particularly the case with the substances dealt with here. Z. K.

Filtration of Colloidal Solutions. A New Filter. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1910, 24, 354—367).—The addition of a certain quantity of glycerol to an ethereal-alcoholic solution of cellulose nitrate increases the permeability of the collodion membrane made from such solutions. The membrane, however, is not stable on exposure to the air, as it contracts and glycerol is exuded. If castor oil is added as well as glycerol, a stable membrane is obtained, which does not contract on exposure to the air, and can be preserved for a long time between filter paper in order to keep away moisture. It can be used as an ultra-filter, which works under the pressure of the liquid contained in it, no extra pressure being necessary. To prepare it for use, it is simply soaked in water to dissolve out the glycerol. The solutions which gave the best membranes contained four parts of cellulose nitrate, 3.5 parts of castor oil, and 2.5, 3, 4, and 5 parts respectively of glycerol, the alcohol and ether used to form the solution being in the proportion 10 parts of alcohol to 80 parts of ether.

Experiments on the filtration of colloidal solutions, classified according to the size of the particles (compare Bechhold, *Abstr.*, 1908, ii, 24, 823), showed that the smaller the particles, the smaller is the amount of glycerol which should be used to obtain membranes which will retain the particles.

The membranes so made can only be used for the filtration of colloidal solutions containing particles varying in size from those of colloidal arsenic sulphide to colloidal Prussian-blue (compare Bechhold, *loc. cit.*). The author has succeeded in separating colloidal arsenic sulphide from Prussian-blue by filtration through the membrane containing 4 parts of glycerol to 4 and 3.5 parts of cellulose nitrate and castor oil respectively.

T. S. P.

The Action of Chloroform on Lipoid Suspensions. D. CALUGAREANU (*Biochem. Zeitsch.*, 1910, 29, 96—101).—The appearances are described when cholesterol and other lipoids in colloidal solution are shaken with chloroform and other solvents which are not miscible with water. The particles of the lipid increase in size, and in the case of cholesterol lose their crystalline form, and form a kind of precipitate on the surface of the chloroform when this solvent is employed in the experiment. The phenomenon is ascribed to the adsorption of the chloroform on the surface of the lipid, and is contrasted with the phenomena observed when colloidal metals, such as gold and silver, are shaken with mercury. Here no adsorption takes place, and the difference of action is ascribed to the fact that the mercury, in contrast to chloroform, is not soluble in water.

S. B. S.

The System Chlorine-Sulphur Dioxide. ANIRIAS SMITS and N. J. DE MOY (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 339—341).—The nature of this system has been investigated by freezing-point measurements. The melting points of chlorine and sulphur dioxide are -100.45° and -75.6° respectively. The data obtained in the dark indicate a eutectic point at -102.3° , the

composition corresponding with 1.5 mols. % of sulphur dioxide. From the form of the freezing-point curve, the authors conclude that mixed crystals are formed.

Measurements in which the mixtures were subjected to sunlight or the light from a quartz mercury lamp show that sulphuryl chloride is formed very rapidly in these circumstances. A mixture containing 47.1 mols. % of sulphur dioxide, in which equilibrium had been established in sunlight, was found to exhibit initial solidification at -80° , which is very much higher than the temperature corresponding with the freezing-point curve for the system in the dark.

H. M. D.

Critical End-Points in Ternary Systems. ANDREAS SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 342—352).—The gradual changes which the critical solution phenomena exhibit when a third substance is added to a binary system are discussed. The third substance is of such a nature that it does not yield critical end-points with either of the components of the binary system, and is completely miscible with these components in the liquid state. The binary system to which special reference is made is that of ethyl ether-anthraquinone, which has been previously examined in detail, and the third substance is ethyl alcohol.

H. M. D.

Critical Phenomena of the Ternary System Ethyl Ether. Anthraquinone, and Naphthalene. ADA PAIRS (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 353—359).—Experiments have been made to ascertain the nature of the critical solution phenomena which are exhibited when the binary system ethyl ether-anthraquinone is converted into a ternary system by the addition of naphthalene. For small quantities of naphthalene the two critical end-points, which are characteristic of the binary system, are still observable. As the proportion of naphthalene increases, the end-points approximate to one another, and the special region bounded by the critical curves disappears as a result of this approximation when the proportion of naphthalene added amounts to 4.5%.

H. M. D.

The Ternary Systems Alkali-Phosphoric Acid-Water. JON. D'ANS and O. SCHREINER (*Zeitsch. physikal. Chem.*, 1910, 75, 95—107).—The equilibria in these systems have been determined by solubility measurements at 25° in the usual way, and the results are given in tabular form, and also represented graphically.

In the system containing sodium salts, the solid phases met with were the compounds $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Trisodium phosphate dodecahydrate has a transition temperature at $70.75 \pm 0.1^{\circ}$. The corresponding disodium salt has two transition points, the first, represented by the equation $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$, at $35.4 \pm 0.05^{\circ}$; the second, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + 5\text{H}_2\text{O}$, at $48.35 \pm 0.05^{\circ}$. The solubility, in grams anhydrous salt per 100 grams of water, is 46.11 at the former, and 79.00 at the latter, transition point. The region of the acid mono-

sodium phosphate described by previous observers was not reached; it is stable only in the presence of practically pure phosphoric acid.

In the system containing potassium salts, only the three anhydrous salts, K_2PO_4 , K_2HPO_4 , and KH_2PO_4 , were met with. The investigation was difficult owing to the extremely high solubility of the di- and tri-potassium salts. The region within which K_2HPO_4 exists is very narrow, lying between the ratios $K : PO_4 = 6.9 : 4.15$ and $K : PO_4 = 4.8 : 1$, or $K : PO_4 = 1.66 : 1.60$. The region of the acid monosodium phosphate, KH_2PO_4 , H_3PO_4 , described in the literature was not reached.

In the system containing ammonium salts, the compounds $(NH_4)_3PO_4$, $3H_2O$, $(NH_4)_2HPO_4$, and $NH_4 \cdot H_2PO_4$, were met with as solid phases. The diammonium salt exists only within narrow limits of concentration.

For all three alkalis, the systems in which the solution and the solid phase have the ratio $PO_4 : \text{alkali} = 1 : 1$ represent an absolute minimum in the solubility of these compounds; in other words, the solubility of the monoalkali phosphates is increased by the addition of alkali as well as of phosphoric acid.

G. S.

Stability of the Two Crystalline Modifications of Phenol. GISELA TAMMANN (*Zeitsch. physikal. Chem.*, 1910, 75, 75—80).—The conditions of stability of the different forms of phenol have been further investigated (compare Abstr., 1909, ii, 983) by an improved experimental method.

As a preliminary to the preparation of phenol II (the denser modification) in open vessels at atmospheric pressure, curves are plotted giving the temperatures and corresponding pressures at which the velocity of transformation of phenol II to phenol I in the presence of both phases becomes appreciable. Further, the conditions under which spontaneous transformation of phenol II to phenol I (ordinary phenol) takes place are tabulated. At -39° , the latter change takes place at 154 kilog./cm.² pressure; at -28.2° , 410 kilog.; at $+3.5^\circ$, 1025 kilog., and at 29° , 1625 kilog. At -80° , no appreciable change takes place in a considerable time at atmospheric pressure.

Phenol II was prepared at 15° under a pressure of 3000 kilog./cm.². The cylinder of nickel steel containing it was then cooled at -80° , and the pressure gradually lowered to 1 kilog. After some further manipulations, phenol II was obtained, and freed from its wrappings in a mixture of light petroleum and chloroform cooled to -80° , in which it sank, whereas a piece of ordinary phenol floated in the mixture. The diminution of volume when phenol I changes to phenol II is 0.06 cm. per gram.

G. S.

[Temperature-coefficient of Chemical Reaction Velocities.] Correction. MAX TRAUZ (*Zeitsch. physikal. Chem.*, 1910, 74, 747).—A correction is applied to one of the author's formulae on this subject (compare this vol., ii, 24) which simplifies it and renders it more accessible to experimental investigation.

G. S.

Slow Combustion of Sulphur. MAX BODENSTEIN and WALTER KUHO (*Zeitsch. physikal. Chem.*, 1910, 75, 30—47).—Ewan (Abstr., 1895, ii, 213) found that the rate of oxidation of sulphur is proportional to

the square root of the pressure of the oxygen, but the present authors have obtained entirely different results.

The sulphur was heated at constant temperature (252°) with oxygen in a glass tube for definite intervals, the mixture of oxygen and sulphur dioxide transferred to a measuring vessel, and the proportion of sulphur dioxide in the mixture determined by observation of the pressure before and after absorption of the sulphur dioxide with an iodine-potassium iodide solution.

The rate of reaction is directly proportional to the pressure of the oxygen, and is roughly proportional to the surface of the sulphur. The rate increases in the ratio 1.87:1 for a rise of temperature of 10° . From these observations the conclusion is drawn that the controlling reaction is a chemical one, which takes place in the adsorption layer on the surface of the sulphur. The excellent agreement of the velocity coefficients shows that the sulphur dioxide, which must accumulate in the adsorption layer, has no influence on the reaction velocity, and the authors show that this can be reconciled with their view as to the mechanism of the reaction.

At 159° , the temperature at which Ewan worked, the rate of oxidation of sulphur is extremely slow, and this observer must therefore have measured some other reaction. His heated sulphur was near a soda-lime tube (used for absorbing the sulphur dioxide), and it is suggested that the sulphur distilled over to the soda-lime, forming polysulphides and thiosulphate, which were very rapidly oxidised by the oxygen.

G. S.

Specific Stereochemical Behaviour of Catalysts. KASIMIR FAJANO (*Zeitsch. physikal. Chem.*, 1910, **75**, 232—234. Compare this vol., ii, 599).—The point at issue between the author and Rosenthaler (this vol., ii, 232) requires further experimental investigation.

G. S.

Dead Spaces. RAPHAEL ED. LIESEGANG (*Zeitsch. angew. Chem.*, 1910, **23**, 2124—2125).—A small glass tube, open at both ends and filled with a 10% jelly containing sodium chloride, is immersed in a solution of silver nitrate. When the diffusion of the silver nitrate and the precipitation of silver chloride is complete, a clear space of several mm. is left in the centre of the tube, where no precipitation has occurred. It contains silver nitrate but no chloride. This "dead space" is due to the fact that the sodium chloride has diffused away to the places where precipitation of silver chloride has occurred. Such a "dead space" is not formed when the substance dissolved in the jelly is not diffusible, for example, when the jelly contains albumin and the tube is immersed in metaphosphoric acid.

If the jelly contains potassium dichromate instead of sodium chloride, a "dead space" is still formed in the middle of the tube. The silver chromate deposit is not continuous, however, as in the case of silver chloride, but in the form of rings with clear spaces between (the ordinary Liesegang phenomenon). The latter clear spaces are not identical with the "dead space" in the centre of the tube, if a "dead space" is defined as one where no chemical reaction has taken place,

since silver chromate has been formed in them, and while in supersaturated solution has diffused to the places where precipitation has taken place. These results make it doubtful whether the phenomena observed by Liebreich (Abstr., 1891, 1150) are really due to the occurrence of "dead spaces."

The importance of these phenomena in connexion with, for example, the occurrence in many bones of zones poor in lime is pointed out.

T. S. P.

Repeating Figures in the Atomic Weight Values. F. H. LORING (*Chem. News*, 1910, 102, 228—229).—In the International Tables for 1911 there appears to be a tendency for the figure in the unit's place to recur in the second place of the decimals, for example, Ag = 107.87, Fe = 55.85, but this may be accidental.

G. S.

A New Valve. AUG. KUMM (*Chem. Zeit.*, 1910, 34, 1136).—A valve for preventing the return of water into vessels while being exhausted by the filter-pump is described. A glass rod is supported on the mouth of a vertical glass tube by means of an expansion covered with indiarubber. During suction the valve is raised, but if the pump is stopped, or if water returns, the rubber-covered expansion makes a tight joint with the tube.

C. H. D.

Modified Drying Tube. EDWIN DOWZARD (*Amer. J. Pharm.*, 1910, 82, 509—510).—By inserting a stopcock in the lower part of a Pelligot drying tube, the exhausted sulphuric acid may be removed and replaced with fresh acid by suction at the side-tube without dismantling connected apparatus. A small test-tube is suspended under the stopcock to catch drops of exuding acid.

T. A. H.

Extraction Apparatus. R. P. NOBLE (*J. Amer. Chem. Soc.*, 1910, 32, 1533).—A form of apparatus for the extraction of substances by means of mixed solvents is described. It consists of a glass tube, the bottom of which is connected with a syphon tube, to the upper end of which a side-tube is attached. The substance to be extracted is contained in a cartridge, and the solvent is removed by actuating the syphon. The apparatus avoids the use of any stopcock.

H. M. D.

Lecture and Laboratory Apparatus. JAMES A. SCHOFIELD (*Austral. Assoc. Report*, 1909, 167—172).—The following forms of apparatus are described. I. Apparatus for showing the composition of nitrous and nitric oxides. Instead of the original method devised by Davy for heating sodium in the gas, the sodium is contained in a deflagrating spoon and fired electrically. The gas is confined in one limb of a manometer, the electrical connexions passing through a rubber cork at the top of the tube. II. Apparatus for the preparation of ammonium hydroxide solution, concentrated and dilute, from liquid ammonia. III. A rapid form of condenser for distilled water. The condenser is practically a reversed tubular boiler, nine $\frac{3}{4}$ -in. tin tubes 1 ft. long forming the condenser. IV. A cheap demonstration balance. Fitted to the centre of the beam, and projecting above it, is a light aluminium

pointer, about 21 inches long, playing over a cardboard scale. The scale and pointer are turned towards the class, the ordinary scale and pointer being towards the lecturer. The aluminium pointer is counter balanced by a binding screw clamped on to the ordinary pointer. V. Nickel crucibles for the Laurence Smith method of determining alkalis in silicates. These crucibles are used for the decomposition of silicates with calcium carbonate and ammonium chloride, and give the same results as platinum ones.

T. S. P.

Apparatus for Laboratories and Lecture Experiments. JOHANNES THIELE (*Annalen*, 1910, 376, 279—285).—Chlorinations and brominations, and also the detection of feeble fluorescence, can be accomplished very successfully in the light of an arc lamp instead of in sunlight. Apparatus for the demonstration of the production of water in quantity from its elements and of the combustion of nitrogen are described, and also electrically heated filter funnels, boiling point apparatus, etc.

Many lecture experiments, in which the reagents are heated to boiling, can be performed in very much shorter time by placing a little of the not too dilute reagents in an upright cylinder and adding much boiling water. The hydrolysis of ferric alum, the formation and decomposition of copper hydride, the hydrolysis of carbonates and of sucrose, the decomposition of mercuric nitrate, and the hydrolysis of ferric chloride are thus readily demonstrated.

G. S.

Inorganic Chemistry.

Preparation of Pure Hydrogen Peroxide for Medical Purposes. OTTO SCHMATOLLA (*Pharm. Zeit.*, 1910, 55, 888—890).—The method used consists essentially of (1) solution of commercial barium peroxide in hydrochloric acid, phosphoric acid being added to precipitate metals such as iron; (2) precipitation from the solution of hydrated barium peroxide by means of sodium hydroxide; and (3) preparation of the solution of hydrogen peroxide in the usual way by the addition of the hydrated barium peroxide to sulphuric acid.

T. S. P.

Formation of Hydrogen Peroxide. K. V. CHARITSCHOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 900—904).—Papers prepared with cobalt naphthenate are very sensitive to hydrogen peroxide, turning from pink to olive-green (compare this vol., ii, 238). In bright sunlight or by a rise of temperature they become still more sensitive, it being possible to detect one part in 1,000,000 of water.

Water containing oxygen when exposed to bright sunlight gives the hydrogen peroxide reaction after the following intervals: at 9—22° after twelve days; 19—31° after eight days; 20—41° after seven days.

If the oxygen is replaced by air, no hydrogen peroxide is formed. In similar experiments with radioactive barium chloride, and also the nitrates of barium, lead, thorium, uranium, and bismuth, hydrogen peroxide was formed only in the presence of radioactive barium salt and of lead nitrate. When, however, the experiment was made in the dark, even radioactive barium produced a negative result; it is therefore considered that it is not the radium emanation which induces the reaction $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$, but that the radium salt acts as a catalyst.

Hydrogen peroxide is also formed on the surface of moist, porous substances, such as wood, asbestos, and so forth. Z. K.

Formation of Hydrogen Peroxide in the Combustion of Detonating Gas. K. V. CHARITSCHKOFF and AMBARDANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 904).—Using the cobalt naphthenate papers (compare preceding abstract), hydrogen peroxide was detected in the products of combustion of detonating gas, 0.000476 c.c. hydrogen peroxide being produced from the combustion of about 25 litres of hydrogen in oxygen.

Hydrogen peroxide could not be detected in the combustion of benzene or of alcohol. Z. K.

Colour of Iodine Solutions. JOEL H. HILDEBRAND (*Zeitsch. physikal. Chem.*, 1910, 74, 679–682).—The author answers some adverse criticisms of Waentig (this vol., ii, 117) on his and Glascock's work on this subject (compare Abstr., 1909, ii, 225). In particular, the standard solution (for comparison purposes) was prepared by adding to the violet solution of known iodine concentration sufficient of the "active" solvent to be investigated to change the violet colour completely to brown, so that Waentig's objection that the authors had assumed the colour of the additive compound to be the same for all the solvents used is not valid. G. S.

Solubility of "Insoluble" Sulphur (S_{μ}). ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1910, 75, 235–244. Compare Abstr., 1910, i, 228).—When amorphous insoluble sulphur, S_{μ} , is treated with carbon disulphide or carbon tetrachloride, a small proportion of it (usually not exceeding 3 per cent. with carbon disulphide) goes into solution, the proportion depending on the time of action, the temperature, and the nature of the solvent, but being independent of the amount of solvent. This is ascribed to a partial change of S_{μ} to soluble sulphur, S_A , under the influence of the solvent. Further, a small amount of S_{μ} , under ordinary conditions less than 1 in 1000, goes into solution unaltered, probably in the colloidal form.

The author maintains the accuracy of his figure, 118.95, for the melting point of monoclinic sulphur. G. S.

The Supposed Nitrososulphonic Acid of Raschig (Sabatier's Nitrosodisulphonic Acid) and the Theory of the Lead Chamber Process. WILHELM MARCHOT (*Zeitsch. angew. Chem.*, 1910, 23, 2113–2114).—Raschig's theory of the lead chamber

process assumes the intermediate formation of nitrososulphonic acid, $\text{HO}\cdot\text{NO}\cdot\text{SO}_3\text{H}$ (compare Abstr., 1908, ii, 30), the solution of which in concentrated sulphuric acid has a blue colour; in more dilute acids there is a slight red colour. This blue colour is also produced by the action of a mixture of sodium nitrite and mercury on sulphuric acid, but disappears after a time, nitric oxide being evolved.

The author finds that the solution of nitric oxide in pure sulphuric acid is colourless; if, however, the sulphuric acid contains iron, a red coloration is produced. The red coloration observed by Raschig in some experiments of his (Abstr., 1905, ii, 23, 700), and also a solubility of nitric oxide in sulphuric acid considerably greater than that observed by the author, are due to the use of impure sulphuric acid. The "purple acid" from the Gay Lussac tower is nothing more than a solution of the ferrous or ferric sulphate compound of nitric oxide.

The brown coloration produced by the solution of nitric oxide in an aqueous solution of ferrous sulphate is not due to the formation of

ferrous nitrososulphonate, $\text{ON}\langle\begin{smallmatrix} \text{O} \\ \text{SO}_3 \end{smallmatrix}\rangle\text{Fe}$, as assumed by Raschig,

since the same colour is produced with ferrous chloride and ferrous hydroxide. The compounds formed contain one molecule of nitric oxide to one atom of iron, and are probably of the type $\text{NO}\cdot\text{FeCl}_2$ (compare Abstr., 1907, ii, 93). For similar reasons it is probable that Raschig's copper nitrososulphonate does not exist (compare this vol., ii, 956).

Thus the existence of a nitrososulphonic acid has still to be proved. The same objections may also be raised to Sabatier's nitrosodisulphonic acid.

T. S. P.

Revision of the Atomic Weight of Nitrogen. Exact Analysis of Nitrogen Tetroxide. PHILIPPE A. GUYE and C. DROUJININE (*J. Chim. Phys.*, 1910, 8, 473—514).—The atomic weight of nitrogen has been determined by decomposing weighed quantities of nitrogen tetroxide with incandescent iron wire.

The possibility of obtaining pure nitrogen tetroxide for the purpose depends on the following considerations. Nitrogen trioxide is easily oxidised at the ordinary temperature to tetroxide. The tetroxide is not further attacked by oxygen, although it is oxidised by ozone; on the contrary, the pentoxide undergoes spontaneous decomposition into tetroxide and oxygen. The equilibrium between nitrogen tetroxide and nitric oxide plus oxygen has been determined, and the result shows that the dissociation of tetroxide is negligible under the conditions of experiment. The calculations are not affected by the question as to whether the formula of the tetroxide is NO_2 or N_2O_4 . The vapour-pressure curves of nitric oxide, nitrogen tetroxide, and nitrogen trioxide (prepared by Baker's method) were determined in an apparatus specially designed to protect the surface of the mercury by a buffer of air from corrosion by the tetroxide. The curves, which are in accord with those of Ramsay and Young, indicate that although the tetroxide should be easily separated from nitric oxide by distillation, the removal of trioxide would be difficult. Accordingly, the tetroxide was prepared by mixing purified and carefully dried nitric oxide with

excess of purified oxygen, and was distilled in a vacuum at least ten times in presence of free oxygen, precautions being taken to free the final product from dissolved oxygen. The absence of traces of trioxide was inferred from the colourless nature of the liquid product. Throughout the manipulations, phosphoric oxide was used to exclude moisture.

The decomposition apparatus consisted of an oval bulb placed with its major axis horizontal, and provided with a stopcock at the top and a tubulure for condensing the gas at the bottom. A spiral of iron wire which traversed the bulb could be heated electrically. It was prepared for use by alternate oxidation and reduction in a low pressure current of dry hydrogen.

From one to two grams of dry nitrogen tetroxide of f. p. -9.6° were distilled into the bulb, and solidified in the tubulure by a freezing mixture. The bulb, having been evacuated and closed, was allowed to warm up, and weighed. After passing the current and removing the residual nitrogen by the pump, the bulb was weighed again.

The mean of seven determinations gives 14.010 as the atomic weight of nitrogen, or neglecting the two first determinations, the remaining five give a mean value 14.009 ($O=16$). Considering the possible sources of error, the atomic weight could not be less than 14.005, and probably not less than 14.008.

The values obtained are in good agreement with those deduced from analyses of nitrous oxide by Guyot (14.0107) and analyses of nitric oxide by Gray (14.0097), but are opposed to those recently calculated by Richards from analyses of silver nitrate, namely, 13.990 to 14.002. The authors consider that the various direct measurements of nitrogen-oxygen ratios are more trustworthy and agree better amongst themselves than the indirect (silver) values, and that it would be reasonable to make the atomic weight of silver depend on the directly determined value for nitrogen, since this is supported by the physical constants of nitrogen.

R. J. C.

Formation of Nitric Oxide in the High Tension Arc.
FRITZ HABER, ADOLF KOENIG, and E. PLATOU (*Zeitsch. Elektrochem.*, 1910, 16, 789—796).—The apparatus and method of experiment have been described in previous papers (Abstr., 1908, ii, 34, 940). Two sets of experiments were made. In the first set, the length of arc and the current (0.27 ampere) were kept constant, and the pressure of the air varied. The results show a very decided maximum yield at 150 mm., the gas leaving the arc containing 8.16% of nitric oxide at this pressure. The second set was designed to determine the relationship between the energy consumed in the arc and the quantity of nitric oxide produced. Owing to the distortion of the voltage curve by the discharge through the gas, the curves of voltage and current are not in the same phase, which introduces some difficulty in the measurement of the energy used in the arc. The methods of measurement are described in detail. The best yield in twenty-four experiments with air at 140 mm. pressure was 57 grams of nitric acid per kilowatt-hour, with 3.4% of nitric oxide in the gas leaving the arc.

T. E.

Formation of Nitric Oxide from Air by means of High Frequency, Alternating, Electrical Discharges. FRITZ HABER and E. PLATOU (*Zeitsch. Elektrochem.*, 1910, 16, 796—803).—The electrical measurement of the energy consumed in an unsteady arc produced by an high frequency, alternating current is impossible. The authors have, therefore, measured it by immersing the apparatus in which the discharge occurs in a calorimeter consisting of a Dewar's tube filled with paraffin oil. The platinum resistance thermometer also serves as a stirrer, and the hot gases leave the discharge tube through a silver tube filled with silver filings, which is immersed in the oil and serves to cool them. The discharge takes place between platinum wires placed closed together at their lower extremities and diverging at their upper ends. Good results are only obtained when considerable quantities of energy are used in the arc, and when it is well spread out in a fan-shape. With a current of about 500 periods per second, and air at atmospheric pressure, the yield is as high as 54 grams of nitric oxide per kilowatt-hour; with about one hundred times higher frequency, slightly worse results were obtained (48.7 grams of nitric acid per kilowatt-hour), whilst diminishing the pressure to 387 mm. reduced the yield to about 20 grams. The lower yields are, however, ascribed to the tendency of the arc to hang to one spot on the platinum wires instead of travelling along them, and the authors think that neither pressure nor frequency have any specific influence on the yield obtainable. T. E.

Yield of Nitric Oxide in the Combustion of Air in the Cooled, Direct-current Arc. WILHELM HOLWECH and ANTON KOENIG (*Zeitsch. Elektrochem.*, 1910, 16, 803—810).—An iron wire, 2 mm. diameter, surrounded by a quartz tube served as cathode. The anodes were water-cooled, copper capillary tubes of from 0.5 to 3 mm. bore. The electrodes were usually placed 2 to 5 mm. apart, and the air was drawn off through the capillary tube by means of an air pump; the arc is thus drawn into the cold capillary tube, and the greater part of its length, which varies with the rate at which the air flows, is within the tube. The cathode was not heated as in Holwech's experiments with the same arrangement (this vol., ii, 578), but this had no effect on the results. The yields are always better when the capillary anode is vertically below the cathode, and the air, therefore, drawn downwards, than it is when their positions are reversed. The yield increases with the velocity of the air current (the percentage of nitric oxide in the gas, of course, decreases); with the 0.5 mm. capillary a yield of 74.3 grams of nitric acid per kilowatt-hour was obtained, using air, with 1.94% of nitric oxide in the gas, the arc taking 0.29 ampere at 290 volts. The best results were obtained with the 2 mm. capillary tube, 84.8 grams of nitric acid per kilowatt hour being reached with 2.3% of nitric oxide in the gas, a current of 0.2 ampere, and 280 volts. Attempts to concentrate more energy into the arc gave worse results; reversing the poles and using alternating current also were less successful. T. E.

Formation of Nitric Oxide from Air in the Arc under Pressure. FRITZ HABER and WILHELM HOLWECH. (*Zeitsch. Elektrochem.*, 1910, 16, 810—813).—The arc is formed in a vertical steel tube between a cooled copper cathode and an iron anode placed respectively at the top and bottom of the tube. The air is blown in at the bottom tangentially to the walls of the tube. In one arrangement, cold air was used, in another it was heated by passing over the outside of the steel tube before entering it. With the first arrangement, 0.55 to 1.5 ampere at 700 to 2075 volts were used, and pressures varying from 2 to 21 atmospheres. The best yield was 76 grams of nitric acid per kilowatt-hour with 2 atmos. pressure and 0.36% of nitric oxide. The same yield was obtained at 11 atmos. with only 0.29% of nitric oxide in the gas. With pre-heated air, using currents of 0.5 to 0.6 ampere and 1200 to 1460 volts, the yields were better, 82.8 grams of nitric acid per kilowatt-hour being obtained with 4 atmos. pressure and 0.7% of nitric oxide. At higher pressures, the yields were rather lower.

T. E.

Formation of Nitric Oxide during the Combustion of Hydrogen. A. WOLOKITIN (*Zeitsch. Elektrochem.*, 1910, 16, 814—826).—The experiments of Haber and Coates (Abstr., 1909, ii, 997) on the formation of nitric oxide during the combustion of carbon monoxide in mixtures of oxygen and nitrogen are extended to hydrogen, using the same apparatus and methods of experiment. The results are very similar; the combustion of hydrogen in air at the ordinary pressure yields no nitric oxide; when the pressure is increased to 20 atmospheres or more, about 0.3 mol. of nitric oxide is formed per 100 mols. of water. With a mixture of equal volumes of oxygen and nitrogen, the yield is small at low pressures, but increases with the pressure, nearly 3 mols. of nitric oxide per 100 mols. of water being obtained at 15 atmos. pressure. Further increase of the pressure up to 50 atmos. produces but little further increase in the yield. A mixture of oxygen and nitrogen with 80% of the former behaves in much the same way as the mixture of equal volumes. The theoretical calculation of the yield, made in the manner adopted by Haber and Coates, indicates a maximum yield of about 4 mols. of nitric oxide per 100 mols. of water, using a mixture of equal volumes of oxygen and nitrogen; the actual yields are less than the theoretical ones, whereas Haber and Coates obtained the opposite result with carbon monoxide.

T. E.

The Behaviour of Nitrous Gases towards Water and Aqueous Alkalies. FRITZ FOERSTER and J. BLICH (*Zeitsch. angew. Chem.*, 1910, 23, 2017—2025. Compare Abstr., 1908, ii, 941, 1031).—The rate of oxidation of nitric oxide by air under different conditions has been determined by absorbing the product in sodium hydroxide and determining the ratio of nitrite to nitrate formed.

In the authors' apparatus, the gases issuing from the large oxidation chamber pass through two vessels containing water, after which the mixture contains nitric oxide as well as peroxide. The third vessel

contains sodium hydroxide. Lengthening the path between the water and alkali increases the completeness of the oxidation, but no improvement is brought about by interposing heated glass spirals. Experiments in which air and nitric oxide pass together into a heated vessel containing broken glass show that the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2\text{O}$ proceeds less rapidly as the temperature rises. This result has also been observed by Bodenstein, and is best explained by the assumption that a molecular oxide is first formed: $\text{NO} + \text{O}_2 \rightarrow \text{NO}\cdot\text{O}_2$, $\text{NO}\cdot\text{O}_2 + \text{NO} \rightarrow 2\text{NO}_2$ (compare Raschig, *Abstr.*, 1907, ii, 455).

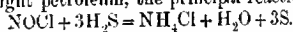
The experiments also show that alkalis absorb nitrogen trioxide more rapidly than nitrogen peroxide. It appears probable that in a partly oxidised mixture the equilibrium $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ exists, although the quantity of trioxide is small, and that the water absorbs the gases in this form (compare Le Blanc, *Zeitsch. Elektrochem.*, 1905, 12, 544). When pure liquid nitrogen trioxide is added to sodium hydroxide solution at -22° , it is instantly absorbed, whilst liquid nitrogen peroxide only reacts slowly.

C. H. D.

The Reduction of Nitrosyl Chloride. HUMPHREY O. JONES and J. K. MATHEWS (*Proc. Camb. Phil. Soc.*, 1910, 15, 529—530).—When nitrosyl chloride and ethyl mercaptan react in ethereal solution at -80° , small quantities of hydroxylamine hydrochloride are formed. The action of other reducing agents on nitrosyl chloride has therefore been studied, but the formation of hydroxylamine hydrochloride has only been observed when nitrosyl chloride and hydrogen are passed over reduced platinum, cooled in a freezing mixture. Even in this case the hydroxylamine hydrochloride only forms 5% of the ammonium chloride produced. When the contact substance is nickel, the product is ammonium chloride.

With palladium, the products at the ordinary temperature are palladium chloride, nitric oxide, and nitrogen; at higher temperatures ammonium chloride is formed.

Hydrogen sulphide and nitrosyl chloride interact at a low temperature in ether or light petroleum, the principal reaction being



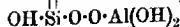
C. H. D.

Presence of a Small Quantity of Carbon Monoxide in the Atmosphere of Coal Mines. P. MAHLER and J. DENET (*Compt. rend.*, 1910, 151, 645—647. Compare this vol., ii, 607; Boudouard, *Abstr.*, 1909, ii, 234).—Carbon monoxide has been found to occur in the air of well-ventilated coal mines to the extent of about 0.002% by volume; the maximum amount found was 0.004%. Iodic anhydride was employed to estimate the carbon monoxide, and precautions were taken to avoid the influence of traces of dust or unsaturated hydrocarbons.

W. O. W.

Silicates with Linked Silicon Atoms. WILHELM MANCHOT (*Ber.*, 1910, 43, 2603—2604).—In his lecture before the German Chemical Society (this vol., ii, 780), W. Pukall represents the constitution of

“kaolin-acid” as $\text{OH}\cdot\text{Si}\cdot\text{O}\cdot\text{O}\cdot\text{Al}(\text{OH})_2$, there being a double linking



between the two atoms of silicon. A similar constitution is given to kaolin.

The author points out that such substances should evolve hydrogen when treated with hydrofluoric acid, or with hydrofluoric acid followed by alkali (compare Abstr., 1905, ii, 165; 1908, ii, 46), and that therefore the above formula is an impossible one. Moreover, the doubly linked atoms of silicon would indicate that a reduction of silicic acid had taken place in the preparation of the compound, whereas no reduction could take place according to the method of preparation described by Pukall. Such a linking would be broken by the action of alkali and not be stable, as postulated by Pukall.

T. S. P.

Preparation of Argon. GEORGES CLAUDE (*Compt. rend.*, 1910, 151, 752-753).—Details are given of a laboratory method for preparing argon at the rate of 2-3 litres per hour. The compressed oxygen of commerce, when obtained from liquid air, contains over 3% of argon, and is a convenient source of this element. The oxygen is absorbed by reduced copper, and the small amount of nitrogen by heated magnesium.

W. O. W.

Determination of the Velocity of Sound in Potassium Vapour and the Monatomicity of its Molecules. WILHELM WEIZ (*Ann. Physik.*, 1910, [iv], 33, 951-970).—Measurements of the velocity of sound in potassium vapour have been made by Quincke's resonance method at 850°. The vapour was contained in a steel tube surrounded by a wider porcelain tube, which was heated electrically. The one end of the steel tube was closed by a thin mica plate serving as a vibrating resonance diaphragm. In order to obtain satisfactory results with this at the high temperature, it was found necessary to protect the inner surface with a thin layer of silver. The other end of the tube was formed by a piston which could be moved up and down, and by this means the length of the column of vapour could be varied. The distances between successive positions in which resonant vibration was obtained were determined, and compared with the corresponding lengths for air. The measurements give 1.77 for the ratio of the specific heats. From this, the author concludes that the vapour of potassium consists of monatomic molecules.

H. M. D.

Equilibrium in the System: Potassium Iodide, Iodine, and aqueous Alcohol. CHARLES L. PARSONS and H. P. CORLISS (*J. Amer. Chem. Soc.*, 1910, 32, 1367-1378).—The solubility of iodine and potassium iodide in aqueous-alcoholic solutions containing varying amounts of potassium iodide and iodine respectively has been measured at 25°. In an alcohol-water mixture containing 60% of alcohol, two solubility curves are obtained, which intersect at a point corresponding with a solution containing 20.0% of potassium iodide and 72.5% of iodine. Similar results were obtained with a solvent containing 40% of alcohol, the point of intersection of the two curves corresponding in this case with 25% of potassium iodide and 76.8% of iodine. The limiting solutions

indicated are those which are simultaneously saturated with respect to iodine and potassium iodide. The solubility data afford no evidence of the formation of solid polyiodides, and the absence of these has been confirmed by analyses of the solid phases in contact with the saturated solutions.

The question of the existence of polyiodides in solution is discussed and experiments are described which show that the iodine and potassium iodide in an aqueous solution of these substances can be partly separated by diffusion. These results are interpreted as indicating that polyiodides are not formed to any appreciable extent. The increased solubility of iodine in an iodide solution as compared with pure water is attributed to the high solvent power of the dissolved solid.

H. M. D.

Sodium Tellurides. GIOVANNI PELLINI and E. QUERCIGH (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 350—356. Compare Tibbals, *Abstr.*, 1909, ii, 728).—With a view to throwing further light on the analogy between tellurium, sulphur, and selenium, the authors have investigated the sodium tellurides by thermal methods. The cooling curves of mixtures of the two elements were observed in an atmosphere of nitrogen, a quartz vessel being employed, and the temperatures measured by means of a platinum and platinum-rhodium couple. The results obtained are also exhibited in a curve, from which it follows that under the conditions of the experiment three compounds can exist, namely, Na_2Te , Na_3Te_2 , Na_3Te_3 . Only the first melts unchanged. It is whitish in colour, but rapidly darkens in the air, and is very deliquescent. The other two have a grey, metallic aspect. In these circumstances it was not possible to obtain the compound Na_2Te prepared by Tibbals (*loc. cit.*). The formulæ of these tellurides differ from those of the selenides (compare Mathewson, *Abstr.*, 1907, ii, 682) and sulphides, except in the case of the type Na_3Te .

R. V. S.

The Equilibrium Diagram of the Silver-Sodium Alloys. E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, 68, 301—306).—Sodium does not react appreciably with silver below 700° . The alloys may be prepared in all proportions by fusion in a current of nitrogen, and separation into two liquid layers does not take place. The freezing-point curve falls rapidly at first, then slowly, and then, from 90 atomic % Na, very rapidly. The eutectic point lies not more than 0.1° below the freezing point of sodium. Solid solutions of sodium in silver are formed up to 13 atomic % Na.

C. H. D.

Photo-Halides. I. WILLEM REINDERS (*Chem. Weekblad*, 1910, 7, 961—973).—Crystalline photo-chlorides of silver have been prepared by crystallising silver chloride from dilute aqueous solutions of ammonia in presence of sunlight. The crystals were indigo-blue in colour, the depth of tint depending on the intensity of the light and the duration of the crystallisation. The darkest crystals contained about 1% of free silver. Exposure under blue glass during crystallisation

tion did not affect the colour of the resulting crystals, but with green or yellow glass the tint was much lighter, and with red glass colourless crystals were formed. During exposure to light for several hrs. the colour of the crystals changed to reddish-brown, and they became opaque. Longer exposure to light produced a grey colour with metallic lustre. These colour changes are caused by superficial reduction to metallic silver. The free silver present in the photo-chloride is in the colloidal state.

Crystallisation from a solution of colloidal silver was effected by addition of a small proportion of formaldehyde to a saturated solution of silver chloride in ammonia (4*N*), slow reduction to a colloidal solution of silver taking place. In transmitted light, the resulting crystals were light yellow to reddish-brown in colour, whilst in reflected light they were yellow, chocolate-brown, or green. They did not contain more than 1—2% of free silver. In diffused sunlight, they changed slowly in colour from yellow to indigo-blue, with production of intermediate shades of red, reddish-violet, and violet-blue.

A. J. W.

The So-called Emulsion of Silver Iodide. JOHN K. THURMER. *J. Pharm.*, 1910, 82, 507—508).—When silver nitrate reacts with potassium iodide dissolved in a solution of egg-albumin, the water part of the precipitated silver iodide is maintained in colloidal solution. Irish moss mucilage gives fairly good results as a substitute for egg-albumin.

Solutions of gelatin (0.1—0.5%) in water also give good suspensions. In this medium the precipitates at first fall to the bottom of the flask, but permanent, almost perfect suspension can then be obtained by agitation, and the suspension improves on keeping.

T. A. H.

The Tellurides of Silver. GIOVANNI PELLINI and E. QUERCIGHI. *R. Accad. Lincei*, 1910, [v], 19, ii, 415—421).—The mixtures of tellurium and silver are melted in a current of nitrogen. The cooling-point diagram indicates the formation of two compounds, Te and Ag_2Te , the first being marked by a break in the curve at 12° , and the second by a maximum at 959° . There are two eutectic pts., at 351° and 33.3 atomic % Ag, and at 872° and 86 atomic % Ag respectively. The compound AgTe undergoes a transformation at 12° , but a polymorphic change of Ag_2Te , which is identical with the mineral hessite, is not observed.

The alloys are crystalline and metallic in appearance, changing from grey to white as the silver increases. The brittleness diminishes from tellurium to silver.

C. H. D.

The Absorption of Bromine by Lime. W. A. R. WILKS (*Proc. Phil. Soc.*, 1910, 15, 526—528).—Solutions of bromine in carbon tetrachloride react with slaked lime with the formation of a reaction product. Using weak solutions of bromine, the concentration of bromine in the lime increases with the concentration of the solution, the ratio $C_1/C_2^{1/4}$ being sensibly constant, pointing to the

formation of an adsorption product. With more concentrated solution of bromine, the quantity taken up is independent of the concentration and the ratio $\text{Ca}(\text{OH})_2:\text{Br}=4.42:1$, indicating the formation of compound. With dry slaked lime, the ratio soon becomes constant: 14.9:1, the equilibrium concentration of bromine being thus much lower, a result similar to that observed with bleaching powder. The colour of the product increases until the constant concentration is reached.

C. H. D.

Anhydrous Sulphates G. CALCAGNI and G. MANCINI (*Atti Accad. Lincei*, 1910, [v], 19, ii, 422—427).—The double sulphates of calcium and the alkali metals have been studied by D'Ans (Abstr. 1909, ii, 401). The freezing-point curve of mixtures of calcium sulphate and sodium sulphate has now been determined. Pure calcium sulphate decomposes so readily at 1000° that its freezing point cannot be determined, but extrapolation of the curve gives 1375° . Sodium sulphate melts at 887° and undergoes a polymorphic change at 234° ; this transformation is not observed in mixtures containing more than 7% of calcium sulphate. The curve has a single maximum at 949° , corresponding with the compound $3\text{Na}_2\text{SO}_4.\text{CaSO}_4$, an analogue of vanthoffite, $3\text{Na}_2\text{SO}_4.\text{MgSO}_4$. The eutectic point is at 917° and 5% Na_2SO_4 , corresponding with the composition of the mineral glauberite. It is possible that other double salts may exist at lower temperature, especially glauberite and the pentacalcium sulphate.

Between 73% and 82.6% of sodium sulphate, two liquid layers are formed.

C. H. D.

[Calcium Silicides.] ADALBERT KOLN (*Zeitsch. anorg. Chem.*, 1910, 68, 297—300).—A reply to Hünigschmid (this vol., ii, 303) maintaining the accuracy of the author's formulae for the calcium silicides (this vol., ii, 35).

C. H. D.

The Temporary Hardness of Water. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1910, 23, 2025—2029. Compare Abstr., 1908, ii, 453).—The solubility of calcium carbonate in water free from carbon dioxide is lessened by the presence of magnesium carbonate. Experiments are described to determine the influence of magnesium salts and of organic substances on the temporary hardness, but without definite result.

C. H. D.

Preparation of Crystalline Strontium. ANTOINE GUXTE and GALLIOT (*Compt. rend.*, 1910, 151, 813).—A mixture of anhydrous strontium oxide with the calculated amount of aluminium is heated for four hours at 1000° in a steel tube (10 cm. long, 3 cm. diam.), which is placed in an evacuated porcelain tube. On cooling, the inner tube is found to be coated with silver-white crystals of strontium containing 99.4% of the metal. The product has D 2.65 and the yield is 75% of the theoretical.

W. O. W.

Solubility of Strontium Nitrate and Strontium Hydroxide in the Presence of Each Other. CHARLES L. PARSONS and C. L. PERKINS (*J. Amer. Chem. Soc.*, 1910, 32, 1387—1389).—The solubility

data obtained at 25° can be represented by means of two curves intersecting at a point which gives the composition of the solution saturated with respect to both substances. This solution contains 1.76 parts of strontium oxide and 81.06 parts of strontium nitrate per 100 parts of water. The curves are quite similar to those obtained in the case of barium nitrate and barium hydroxide (compare following abstract), and show that no basic nitrates of strontium are capable of existence at 25°.

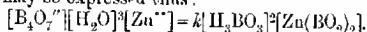
H. M. D.

Solubility of Barium Nitrate and Barium Hydroxide in the Presence of Each Other. CHARLES L. PARSONS and H. P. CONSON (*J. Amer. Chem. Soc.*, 1910, 32, 1383—1387).—These measurements were made to ascertain whether a basic barium salt analogous to the calcium salt, $\text{CaO} \cdot \text{Ca}(\text{NO}_3)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, is capable of being obtained.

The graphical representation of the solubility data for 25° gives two curves meeting at a point corresponding with a solution which contains 5.02 parts of barium oxide and 11.48 parts of barium nitrate in 100 parts of water. This solution is saturated with respect to both $\text{Ba}(\text{OH})_2 \cdot 8\frac{1}{2}\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$. The saturated solutions of the two substances separately contain respectively 4.29 parts of barium oxide and 10.30 parts of barium nitrate per 100 parts of water. The solubility of each substance is increased in presence of the other. The data show that basic nitrates of barium are not formed at 25°.

H. M. D.

The Action of Solutions of Borax on Zinc Salts. FRIEDRICH BORCHERS (*Zeitsch. anorg. Chem.*, 1910, 68, 269—291).—The composition of the precipitate obtained from borax and zinc salts is very variable. The possible equilibria have now been studied in detail. The reaction may be expressed thus:



The borax is employed in most of the experiments as a saturated solution, but also occasionally in the solid form or as a supersaturated solution. For the analysis, a part of the filtrate is precipitated with sodium carbonate to remove zinc, neutralised with standard hydrochloric acid with methyl-orange as indicator, and after boiling to remove carbon dioxide, glycerol is added, and the solution is titrated with potassium hydroxide, using phenolphthalein as indicator.

Boric acid does not react with zinc oxide or hydroxide to form solid zinc borate, although some zinc goes into solution, but boric acid and zinc carbonate react readily.

The largest yield of zinc borate is obtained by adding a concentrated solution of a zinc salt to a slight excess of saturated borax solution. The maximum proportion of borax thus precipitated as zinc borate is 8.6% using solid zinc sulphate. Higher results are obtainable from supersaturated borax solution or solid borax. An excess of zinc salt diminishes the yield, complex zinc salts being formed. Indifferent salts have a similar effect, a large excess of magnesium chloride, for instance, preventing precipitation completely.

If the hydrolysis of the borax is checked by the addition of boric acid, the whole of the borax, and even a part of the added boric acid

may be precipitated by means of a zinc salt. Borax does not produce any precipitate with sodium zincoxide, but by addition of only small quantities of sodium hydroxide the precipitation is rendered more complete. If the zinc borate is removed by filtration, and an excess of sodium hydroxide, followed by zinc sulphate, is added to the filtrate, a further precipitate is obtained, and this process may be repeated until 94% of the borax has been converted into zinc salt. Sodium carbonate has less effect than sodium hydroxide, and the addition of sodium chloride or sulphate then modifies the reaction.

Manganous salts behave similarly to zinc salts.

C. H. D.

Hydrates of Cadmium Nitrate. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 562—567).—Cadmium nitrate, which crystallises from aqueous solution with $4\text{H}_2\text{O}$, can be obtained, like the corresponding silver salt, in the anhydrous state by the evaporation of the hydrate. Contrary to Funk's statement (*Abstr.*, 1899, ii, 209), no salt with $2\text{H}_2\text{O}$ or $6\text{H}_2\text{O}$ could be obtained. At low temperatures, however, a salt with $8\text{H}_2\text{O}$ was produced. The anhydrous salt melts at about 350° , and dissolves in water with development of much heat. The solubility curve of the anhydrous salt, $\text{Cd}(\text{NO}_3)_2$, in the hydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (investigated in the solid condition in Flawitsky's apparatus: *Abstr.*, 1909, ii, 886), has a break beyond the m. p. of the hydrate, 59.5° , descending to 44.5° , which is the eutectic point of the mixture, and corresponds with the composition $\text{Cd}(\text{NO}_3)_2 \cdot 2.65\text{H}_2\text{O}$; the curve then rises continuously to the m. p. of the anhydrous salt, about 350° .

Z. K.

The Binary and Ternary Alloys of Cadmium, Bismuth, and Lead. WILLIAM E. BARLOW (*J. Amer. Chem. Soc.*, 1910, 32, 1390—1412).—From observations of the rate of cooling of the molten alloys, the author has determined the freezing-point curves for the pairs of metals: lead-cadmium and lead-bismuth. By combination of these results with the data obtained in experiments on alloys containing the three metals, the solidification diagram for the ternary system has been deduced.

Lead and cadmium give rise to two curves intersecting in a eutectic point, which corresponds with 82.6% of lead and a temperature of 247.3° . On the cadmium side, the form of the curve points to a slight solubility of lead in solid cadmium, and on the lead side, cadmium appears to dissolve in the solid lead to the extent of about 3%.

Lead and bismuth yield a similar diagram, the eutectic temperature being 124.3 — 124.8° , and the composition corresponding with 56.5% of bismuth. On the bismuth side, the data indicate that bismuth dissolves in solid lead to the extent of about 11%.

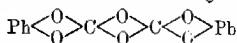
From the very numerous observations which have been made with alloys containing the three metals, a triangular diagram has been constructed. The ternary freezing point is sharply defined at 91.4 — 91.5° , and the composition of the ternary eutectic is given as 40.2% lead, 51.65% bismuth, and 8.15% cadmium.

H. M. D.

Equilibria in the Precipitation of Lead Hydroxide. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 68, 421—424).—When lead oxide is shaken with an alkali halide and water, the whole mass becomes pasty, and it is therefore necessary to approach the equilibrium from the other side. The formation of basic salts may be left out of consideration. The constant $[\text{PbCl}_2][\text{KOH}]^2/[\text{KCl}]^2$ is found to be 0.00073, and for the corresponding reactions with ammonia and methylamine, 0.00082 and 0.00066 respectively. The solubility of lead hydroxide is calculated to be 0.93×10^{-4} . C. H. D.

Basic Lead Carbonates. LEOPOLD FALK (*Chem. Zeit.*, 1910, 34, 937—938).—When lead carbonate is shaken with a solution of basic lead acetate, three parts of carbonate withdraw two parts of oxide from solution, as shown by titration, but the washed precipitate always contains too much carbonate for the formula. If boiled with the basic lead acetate solution the ordinary basic carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, is obtained.

Crystalline and amorphous lead carbonates differ in their chemical behaviour. Thus, whilst the crystalline compound reacts readily with lead oxide in presence of lead acetate, the amorphous modification only reacts very slowly. The formulae $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Pb}$ and

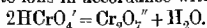


are proposed for the two modifications, and a similar polymerisation is assumed in the case of white lead. Structural formulae for the basic carbonates are proposed.

Hydrogen sulphide only reacts very slowly with crystalline white lead, but rapidly with the amorphous variety. C. H. D.

Solubility of Lead Sulphate and Lead Chromate, and of Mixtures and Oil Colours Containing the two Salts in Dilute Hydrochloric Acid. The Equilibrium between Chromate and Dichromate in Solution. KARL BRICK and PH. STEGMÜLLER (*Arch. K. Gesundh.-Amt*, 1910, 34, 446—483).—Measurements have been made of the solubility of lead sulphate and lead chromate in 0.1N- to 0.6N-hydrochloric acid at 18°, 25°, and 37°. The data for lead sulphate show that, at constant temperature, the solubility is approximately proportional to the concentration of the hydrogen ions. In the case of lead chromate, the solubility in the more dilute solutions is nearly proportional to the hydrogen ion concentration, but in the more concentrated solutions it is more nearly proportional to the square of the concentration of these ions. The increase in solubility with rise of temperature is linear for both salts, the increase per 1° being 2.1% for the sulphate, and 3.5—4% for the chromate.

The equilibria in the solutions have been examined theoretically, and it is shown that the observed differences in the dependence of the solubility of the two salts on the concentration of the acid is due to the formation of dichromate ions in accordance with the equation:



In acid solutions less concentrated than 0.3N, the effect of this change

is not very marked, but in the stronger solutions it results in a considerable increase in the amount of lead chromate dissolved per mol. of acid present. In connexion with the analysis of the equilibrium in solution, measurements were made of the solubility of lead sulphate in 0.1 to 0.4*N*-solutions of sodium chloride and nitric acid, and of lead chromate in 0.1 to 0.6*N*-nitric acid. From these data the following equilibrium constants are calculated: $[H^+][CrO_4^{=2}]/[HCrO_4^{\cdot-}] = 3.7 \times 10^{-7}$, $[H^+]^2[CrO_4^{=2}]/[Cr_2O_7^{\cdot-}] = 3.4 \times 10^{-13}$, $[H^+][Cr_2O_7^{\cdot-}]/[HCr_2O_7^{\cdot-}] = 1.0 \times 10^{-3}$, $[HCrO_4^{\cdot-}]^2/[Cr_2O_7^{\cdot-}] = 2.5$.

Data are also recorded showing the quantities of lead dissolved by 0.1 to 0.4*N*-hydrochloric acid solutions in presence of both sulphate and chromate, and these are supplemented by observations showing the rate at which oil colours containing these two substances are attacked by dilute hydrochloric acid solutions.

H. M. D.

The Ternary System Copper-Antimony-Bismuth. N. COLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Sci. Fis. Mat. Napoli*, 19, ii, 343-449. Compare this vol., ii, 956).—In this system, the results obtained in the examination of the ternary system $Cu_3Sb-Cu-Bi$, the second of the two systems into which the system $Cu-Sb-Bi$ resolves itself. The diagram constructed from them differs from that which was deduced on general grounds, because both copper and bismuth and Cu_3Sb and bismuth form eutectics which practically coincide with bismuth. Photomicrographs of some typical alloys are given. In conclusion, the space of miscibility in the liquid state is discussed, the limits of the space in the two systems being obtained by analysis of the two layers in equilibrium at about 370°, which is very near the initial temperature of solidification of alloys in that region. Uniting the two systems $Cu_3Sb-Cu-Bi$ and $Cu_3Sb-Sb-Bi$ in one diagram, it then becomes possible to exhibit on it the closed curve representing the boundary of the space of miscibility. All alloys within the curve separate into two layers, whilst those outside it are miscible in all proportions.

R. V. S.

Action of Chlorine in Carbon Tetrachloride Solution and of Carbon Tetrachloride on Metallic Oxides. ARTHUR MICHAEL and ARTHUR MURPHY, jun. (*Amer. Chem. J.*, 1910, 44, 365-384).—This investigation was undertaken originally with the object of ascertaining the relation between the position of metals in the periodic system and the behaviour of their unsaturated oxides towards chlorine.

The following experiments were made with a 10% solution of dry chlorine in carbon tetrachloride. With ferrous oxide, a violent action occurs, even when the chlorine solution is cooled to -18°, with formation of ferric oxide and chloride: $6FeO + 3Cl_2 = 2Fe_2O_3 + 2FeCl_3$. Manganous oxide reacts less violently; nickelous oxide reacts readily at the ordinary temperature, but the reaction is not complete for a considerable time; in the case of cobaltous oxide, the mixture must be heated at 100° in a sealed tube in order to complete the reaction. These reactions may be represented by the general equation: $3MO + Cl_2 = M_2O_3 + 2MCl_2$. Stannous oxide reacts violently with the solution.

with formation of stannic chloride and a light brown oxide, probably identical with the oxide, $\text{SnO} \cdot 20\text{SnO}_2$, obtained by Schiff (*Annalen*, 1861, 120, 52) by treating stannic acid with a solution of stannous chloride. Cuprous oxide requires to be heated at 250° with the solution in order to effect a reaction; *cupric oxychloride*, Cu_2OCl_2 , is thus obtained as a dark brown, amorphous powder. Antimony trioxide reacts with the chlorine solution at 100° in a sealed tube in accordance with the equation: $\text{Sb}_2\text{O}_3 + 3\text{CCl}_4 + 2\text{Cl}_2 = 2\text{SbCl}_3 + 3\text{COCl}_2$. In the case of silver oxide, the following reaction takes place at the ordinary temperature: $\text{Ag}_2\text{O} + \text{Cl}_2 + \text{CCl}_4 = 2\text{AgCl} + \text{COCl}_2 + \text{Cl}_2$. The chlorine evidently behaves as a catalyst, since when the oxide is heated with carbon tetrachloride in the absence of free chlorine, carbonyl chloride is not produced until a temperature of about 250° is reached. Lead oxide reacts with the solution at 100° in accordance with the equation: $2\text{PbO} + \text{Cl}_2 = \text{PbO}_2 + \text{PbCl}_2$. Mercuric oxide, although reacting readily with chlorine gas, even at 0° , is not affected by a $\frac{1}{2}^\circ\text{C}$ in the presence of carbon tetrachloride unless the mixture is heated in a sealed tube; the products thus obtained consist of mercuric chloride and some basic chlorides.

When molybdenum dioxide is heated with carbon tetrachloride in a sealed tube at 250° , it is converted into the tetrachloride. Molybdenum trioxide reacts with carbon tetrachloride at 280° with formation of the pentachloride. When the trioxide is heated with a solution of chlorine in carbon tetrachloride at 200° , the product consists of a yellowish-green oxychloride mixed with unchanged trioxide; at 225° , a mixture of yellow and green compounds is obtained, probably consisting of the dioxy-dichloride and the oxytetrachloride; at 240° , the pentachloride is produced. The pentachloride is also obtained when the oxide, Mo_3O_8 , is heated with carbon tetrachloride at 240° . When tungsten trioxide is heated with the chlorine solution, the oxychloride, WOCl_4 , is formed at 240° , and the hexachloride at 280° ; in the absence of free chlorine, reaction does not occur at 240° , but at 280° the hexachloride is produced. Uranium dioxide, if heated with carbon tetrachloride at 250° , yields the tetrachloride, whilst the oxides UO_2 and U_3O_8 , when heated at the same temperature, give the pentachloride. E. G.

Diffusion Phenomena of the Alums. CHARLES L. PARSONS and W. W. EVANS (*J. Amer. Chem. Soc.*, 1910, 32, 1378—1383).—Solutions of alum, when allowed to undergo diffusion into distilled water through a parchment or agar-agar diaphragm, are more or less completely separated into the component simple sulphates. Similar results were obtained at 25° and at 0° . The separation is more complete in the case of the chrome alums than in that of the aluminium alums. The authors draw the conclusion that the dissolved alums are more or less completely resolved into the simple sulphates. H. M. D.

Composition of Some Greek Vases. WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1910, 32, 1259—1264).—A study has been made of the nature and composition of the black glaze of vases of the black-figured and red-figured Attic styles and the red glaze of the Mycenaean style.

The black colour of the glaze of fragments of some Greek vases was found not to be due to manganese, as has been suggested, but to the presence of ferrous iron, probably existing as silicate.

The red colour of the glaze of a fragment of a Mycenaean vase was found to be due to the presence of ferric iron.

A fragment of a vase of the Mycenaean style has been analysed, and the results are compared with those recorded for Attic and Campanian pottery. The Mycenaean pottery contains considerably less silica and much more lime than the other varieties, and yields a large quantity of carbon dioxide. The percentage of aluminium is about the same in each case, but the Campanian ware contains about twice as much ferric iron as the Mycenaean and Attic. The amount of magnesium is about the same in the Mycenaean and Attic varieties, but is much less in the Campanian.

E. G.

The Structure of Cast Iron in the Graphitic Condition. OTTO KRÖHNKE (*Metallurgie*, 1910, 7, 674—679).—When cast iron is transformed into the "graphitic" condition by fusion, the ferrite is removed from the pearlite, whilst cementite and iron phosphide remain unaltered. The graphite retains its position in the mass, but is partly converted into a white or grey substance, graphitite, the composition of which is unknown. White cast iron does not undergo such a change, the constituents being resistant to corrosion. Wrought iron, although containing pearlite in small quantities, does not corrode in this way, the presence of graphite being necessary to produce the requisite electrolytic couples.

C. H. D.

Case-Hardening. SYDNEY A. GRAYSON (*J. Iron Steel Inst.*, 1910, 81, 287—302).—The case-hardening of steel by means of carbonaceous mixtures takes place best at 950—1000°. At 900—950°, diffusion being very slow, a highly supersaturated external layer is produced. Sulphur diffuses in a similar manner to carbon at the same temperature.

C. H. D.

The Crystallography of the Iron-Carbon System. ADOLPH KROLL (*J. Iron Steel Inst.*, 1910, 81, 304—385).—When steel is heated and cooled in an inert gas, relief patterns are obtained indicating the volume changes which have taken place at the critical points. The microscopical examination of etched sections shows that ordinary cementite is hexagonal, but that the carbide entering into solution in γ -iron is regular. A modified equilibrium diagram is proposed, in which a gap exists between two series of solid solutions, one of carbide in γ -iron and one of γ -iron in cementite, the latter solution being identical with troostite. This system is formed in tempering. A theory of the constitution of iron-carbon alloys, based on the crystallographic development, is proposed for the metastable systems, the only stable chemical equilibrium being that of ferrite and graphite.

C. H. D.

The Influence of Sulphur on the System Iron-Carbon. THEODOR LIESCHING (*Metallurgie*, 1910, 7, 565—571).—The distribu-

tion of iron sulphide in alloys of iron and carbon has been studied microscopically. The ferrous sulphide appears in low-carbon alloys in the form of thin films surrounding the crystals of ferrite. When the sulphur exceeds 2% in an alloy high in carbon, two liquid layers are formed, of which the lighter sulphide layer does not contain carbon.

C. H. D.

The Influence of Silicon on the Maximum Solubility of Iron Carbide in γ -Iron. CH. SCHOLS (*Metallurgie*, 1910, 7, 641—646).—The solubility of iron carbide in γ -iron is known to be diminished by the addition of silicon. Thermal and microscopical investigations of alloys prepared from iron and ferro-silicon show that the maximum solubility, which is at 2.2% C in the absence of silicon, is lowered to 1.9% by 1.34% Si, to 1.5% by 1.8% Si, and to 1.2% by 5.6% Si. The eutectic point remains constant at 1120°. The pearlite transformation point is slowly raised by the addition of silicon, but becomes imperceptible above 1.2% C if the alloy contains 5.6% Si, or above 1.5% C in the presence of 4.5% Si.

C. H. D.

Iron, Manganese, and Carbon. JOHN O. ARNOLD and ARTHUR A. READ (*J. Iron Steel Inst.*, 1910, 81, 169—181).—The carbides isolated from alloys of iron, manganese, and carbon by electrolysis show an increase in the ratio of manganese to iron as the proportion of manganese in the alloy is increased, becoming constant in steels containing from 4.98 to 13.38% Mn, afterwards increasing still further. The results do not decide whether double carbides or a mixture of the two carbides are present. Tested by the colour test, carbides of this kind indicate a lower percentage of carbon than pure iron carbide. Up to 10% Mn, the colour is only that due to the iron carbide present, showing that manganese carbide does not give a coloration with nitric acid, D 1.20. Alloys containing 11 or 14% Mn give a higher coloration with nitric acid.

C. H. D.

Some Physical Properties of 2% Chromium Steels. ANDREW McWILLIAM and ERNEST J. BARNES (*J. Iron Steel Inst.*, 1910, 81, 246—267).—The thermal analysis of steels containing 2% of chromium and varying quantities of carbon shows that the critical point A_{c2} is depressed below A_{c1} when the carbon is between 0.2 and 0.5%. The three critical points become identical in steels containing 0.65 or 0.85% C. The saturation point lies between the last two values. The microscopic structure does not indicate the form in which the chromium is present in the steel.

C. H. D.

The A_{c2} Point in Chromium Steel. HAROLD MOORE (*J. Iron Steel Inst.*, 1910, 81, 268—275).—The determination of the critical points of steels containing more than 3% of chromium shows that the position of A_{c1} is progressively raised by the addition of chromium, and that a new critical point appears below A_{c1} . The fact that the new point coincides with the temperature at which the magnetic properties of the steel disappear on heating, proves it to be identical with A_{c2} . An electromagnetic method is employed to determine this point (compare preceding abstract).

C. H. D.

Reduction of Ferric Oxide by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1910, 151, 644-645. Compare this vol., ii, 215).—The authors have studied the speed of reaction between ferric oxide and carbon at low pressures (0.001–8 mm.) to avoid as far as possible the catalytic action of gases. The mode of procedure was similar to that employed when examining the cementation of iron under similar conditions. The conclusion drawn is that carbon is incapable of reducing ferric oxide below 950°, a temperature considerably higher than has hitherto been supposed necessary. •W. O. W.

The System Nickel-Sulphur. KARL BORNEMANN (*Metallurgie*, 1910, 7, 667–674. Compare Abstr., 1908, ii, 292).—The experiments with mixtures high in nickel have been repeated, using magnesia vessels and quartz protecting tubes for the thermo couples. Care being taken to avoid undercooling, the break in the freezing-point curve formerly observed at 1 atomic % S disappears, and only a single series of solid solutions rich in nickel is observed, extending from 0 to 0.5 atomic % S. The complicated transformations in the solid state are confirmed. C. H. D.

Preparation of Anhydrous Chromic Chloride by Bourion's Method. JOSÉ RODRÍGUEZ MOCHELO (*Anal. Fis. Quím.*, 1910, 8, 196–199).—Although chlorine in presence of carbon attacks chromium sesquioxide prepared by gently igniting chromium hydroxide, it is without action on the crystalline sesquioxide or the sesquioxide obtained by ignition at a high temperature. But by Bourion's method (Abstr., 1909, ii, 220) these indifferent substances are rapidly converted into beautifully crystalline scales of chromic chloride; it is only necessary to pass the vapour of sulphur chloride (b. p. 137–139°) over the oxide heated gradually to a red heat, and, after the action is complete, to cool in a current of dry hydrogen chloride. W. A. D.

Uranium Salts. I. and II. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 570–581).—Uranium nitrate gives three hydrates, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and the dihydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, but the nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, does not exist. The hydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, melts at 60–72°, and when further heated just above this temperature, is transformed into the trihydrate, but if heated at a higher temperature a basic salt is formed, which, however, dissolves in water to a yellow solution.

The trihydrate, m. p. 121.5°, forms crystals belonging to the monoclinic system, and can also be obtained by crystallising a strongly acid solution of the sesquihydrate in nitric acid (D 1.4). The dihydrate, m. p. 179.3°, forms small, thick, square plates, probably of the rhombic system, very bright and with a green fluorescence. It is formed when the sesquihydrate is kept for some time in a desiccator at the ordinary temperature, or when the latter hydrate is treated thus at 100°, and the product, which now contains slightly less than $2\text{H}_2\text{O}$, is dissolved in nitric acid, D 1.503, and then allowed to crystallise. When the substance containing less than $2\text{H}_2\text{O}$ is treated

with water, the sesquihydrate separates. Tables and a curve are given for the solubility of the sesquihydrate in water, and the theoretical significance of these are discussed. Contrary to Oechsner de Couinck's statement (Abstr., 1901, ii, 101), the constitution of the solution at 13.5° is about $\text{UO}_2(\text{NO}_3)_2 + 19\text{H}_2\text{O}$. The constitution of the cryohydrate is $\text{UO}_2(\text{NO}_3)_2 \cdot 28.93\text{H}_2\text{O}$ at -18.1° .

Uranium nitrate is one of those salts for which the number representing the degree of dissociation increases with increasing concentration of the solution.

Z. K.

The Solution and Precipitation of Titanic Acid. KARL BORNEMANN and H. SCHIRMISTER (*Metallurgie*, 1910, 7, 646—649).—Contrary to the usual statement in text-books, titanitic acid which has been heated to 1000° is practically insoluble in sulphuric or hydrofluoric acid. If the temperature of ignition does not exceed 700° , solution in concentrated sulphuric acid is complete in fifteen minutes. Hydrofluoric acid has a rather greater solvent power.

Fusion with potassium hydrogen sulphate readily brings about complete solution. It is not necessary to dissolve the product in cold water, for if dilute sulphuric acid (1:2) is used, solution takes place completely even if the liquid is boiled. After fusion with alkali carbonate and solution in hydrochloric acid, the residue is difficult to wash, and readily passes through the filter. This is avoided by the use of sulphuric acid (1:2) instead of hydrochloric acid.

Orthotitanic acid may be precipitated from hot strongly acid solutions by the addition of ammonia without destroying its solubility in dilute acids. When metatitanic acid is dissolved in concentrated sulphuric acid, boiling for more than a few minutes must be avoided, or an insoluble precipitate is formed. No difference in this respect is observed between ortho- and meta-titanic acids.

C. H. D.

Zirconia and Erbium from Titanium Minerals. KARL A. HOFMANN (*Ber.*, 1910, 43, 2631—2636).—Hauy and Wirth have found that the zirconia contained in a number of zirconium minerals is not accompanied by a strange earth (this vol., ii, 713); the author finds that the principal mineral investigated by him, which differs from typical euxenite in that it has a very high titanium content, contains zirconia, which gives some strange lines in the arc-spectrum, and also has a higher equivalent weight than zirconia prepared from zirconium silicate.

The mineral used was euxenite from Brevig, and had the composition:

| CH_3O_2 | TiO_2 | Rare earths. | SiO_2 | PbO | ZrO_2 | Fe_2O_3 | UO_2 | CaO | Loss on heating |
|-------------------------|----------------|--------------|----------------|--------------|----------------|-------------------------|---------------|--------------|-----------------|
| 4.65 | 45.74 | 38.17 | 0.53 | 0.33 | 2.83 | 2.06 | 2.73 | 1.60 | 2.80% |

The rare earths comprised didymium, erbium, and holmium. The zirconia was identified by the preparation of the double fluoride with potassium, and from the mother liquors obtained in the recrystallisation of this salt zirconia was prepared, the arc-spectrum of which showed unknown lines (4519.6, 4322.65, 3682.43, 3662.29, 3253.83,

3194-30, and 3031-32), together with the known lines due to zirconium and titanium. These lines still persisted after the titanium had been removed.

The remainder of the paper deals with neo-erbium compounds. The erbium compounds contained in the rare earths mentioned above are purified from holmium and dysprosium by fractional crystallisation of the ammonium double oxalate (compare Abstr., 1908, ii. 189). Fractional crystallisation of the acetylacetonate compound from alcohol may also be used. Thulium and ytterbium may be readily separated from almost pure erbium sulphate by heating to 845° for ten hours; on treating the residue with water, the less basic portions remain undissolved. The solution is evaporated to dryness, the residue heated to 950° for thirty minutes, and then treated with water, when erbium oxide remains undissolved.

By using the above methods, an erbium material was obtained, which gave a constant spectrum and a constant equivalent weight. After freeing it from impurities derived from the vessel used, a bright rose-red oxalate was obtained, $\text{Er}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. Former analyses have given $9\text{H}_2\text{O}$. On drying in a vacuum over phosphoric oxide, the trihydrate is formed. The oxide results on heating the oxalate to 575° ; it is obtained pure at 845° , and then forms a rose-coloured powder, which does not glow in cathode rays, but gives a green, discontinuous light in the bunsen flame. The reflexion spectrum is not altered by dilution with other oxides when no compound is formed.

Atomic-weight determinations were made by transforming the sulphate into the oxide by heating at 1055° , and gave the mean value 167.68 (three determinations, $O = 16$, $S = 32.07$). At 815° a basic sulphate, $\text{Er}_2\text{O}_3 \cdot \text{SO}_3$, is obtained. T. S. P.

Colloidal Zirconium Silicide. EDGAR WEDEKIND (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 249—251).—Zirconium silicide, obtained by the action of excess of silicon on potassium zirconium fluoride in the electric furnace, has been converted into a colloidal form by Kuzel's method. The finely divided substance was treated successively with dilute acid and alkaline solutions at a temperature of 50 – 60° , the treatment in each case being continued for about twenty-four hours. After a considerable number of such operations, a dark brown colloidal solution of the silicide is obtained. Under the microscope, the solution, which has been kept for some time, appears to be homogeneous, but the want of homogeneity is clearly seen in the ultra-microscope. The colloidal particles move towards the positive pole, and are therefore negatively charged. On the other hand, colloidal zirconium is positively charged, and coagulation takes place when solutions of the metal and of the silicide are mixed. Colloidal zirconium silicide is coagulated by various electrolytes, but in comparison with the colloidal metal, it is not at all readily acted on by solutions of alkali hydroxides. Coagulation of the silicide is also brought about by freezing the solution, and in this respect also it differs from the colloidal solution of zirconium. H. M. D.

Basic Thorium Sulphate. OTTO HAUSER (*Ber.*, 1910, 43, 2776—2778).—The author claims priority to Barre (this vol., ii, 718) in showing that Demarcay's salt (*Compt. rend.*, 1860, 93, 728), $3\text{Th}(\text{SO}_4)_2 \cdot \text{ThO}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$, is really a mixture of $\text{Th}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{ThO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (compare *Abstr.*, 1909, ii, 54). He also confirms Barre's result that at 100° the stable basic sulphate has the composition $\text{ThO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$. At 125 – 180° the stable basic sulphate is $\text{ThO}(\text{SO}_4) \cdot \text{H}_2\text{O}$. The author's and Barre's results show that in moderately dilute solutions of thorium sulphate the basic sulphate, $\text{ThO}(\text{SO}_4)$, is produced, which, according to the temperature, crystallises with one or two molecules of water. In very dilute solutions the sulphate may be completely hydrolysed to the hydroxide. T. S. P.

Preparation of Vanadium. WILHELM PRANDL and BENNO BLEYER (*Ber.*, 1910, 43, 2602—2603. Compare *Abstr.*, 1909, ii, 1022).—Vanadium may readily be obtained by the thermite reaction, using the following mixture: 100 parts of fused and powdered vanadium pentoxide, 49.5 parts of aluminium powder, 20 parts of calcium fluoride. The action is carried out in a magnesia crucible, or, better still, in a box made of fluor spar. In the latter case it is not necessary to add the calcium fluoride to the reaction mixture.

The vanadium regulus obtained is 70–80% of the theoretical quantity, and is 95% pure. The impurity is chiefly oxygen; possibly a lower oxide of vanadium remains dissolved in the excess of vanadium and escapes the reducing action of the aluminium. T. S. P.

Red Platinum as Analogue of Purple of Cassius. LOTHAR WOHLER and A. SPENGLER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 243–249).—Experiments have been made to determine the cause of the red colour which appears when solutions of platinum salts are acted on by stannous chloride. These show that the red substance consists of colloidal metallic platinum in a very fine state of subdivision, and that the formation of this in place of the more usual brown colloidal metal is due to the action of stannic chloride and its products of hydrolysis as protective colloids. The red colloid is also formed when the reduction of platinum salts is effected by means of a solution of phosphorus in ether, if gelatin is added as a protective colloid. The identity of the two red substances has been established by spectroscopic observations.

If the colloidal solution obtained by reduction with stannous chloride is shaken up with ethyl ether or ethyl acetate, the organic solvents take up the red colour, and this is found to be connected with the solubility of stannic chloride in these media, in which it plays the part of protective colloid.

When the aqueous solution is diluted with a large volume of water, or when the ethyl acetate solution is poured into water, a chocolate-brown precipitate is obtained. According to Schnoeder (*Ann. Phys. Chem.*, 1869, [ii], 136, 105), this substance has the composition $\text{Pt}_2\text{Sn}_3\text{O}_{10}$. It is now found, however, that no definite compound is formed, but that the composition of the precipitate varies very considerably with the conditions under which it is produced. Analogous

to purple of Cassius, it appears to be a mixture of colloidal platinum and colloidal stannic acid, and this view is supported by the similarity in the properties of the two substances.

The blood-red colour which appears on reduction of silver nitrate by stannous nitrate in dilute nitric acid solution is similarly due to colloidal silver, and not to the formation of what have been described as silver stannates. On account of the instability of the red colloidal silver, the red solution quickly turns brown, and deposits a reddish-brown precipitate. The red modification of silver cannot be obtained by reduction by means of an ethereal solution of phosphorus.

H. M. D.

Mineralogical Chemistry.

Probable Identity of Podolite with Dahllite. WALDENAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 309—310).—A comparison of the characters and analyses of dahllite (Brügger and Backström, Abstr., 1890, 714) and of podolite (W. Tschirwinsky, Abstr., 1907, ii, 481) [= carbapatite of P. N. Tschirwinsky, 1906] suggests the identity of these minerals. The composition of dahllite was expressed as $2\text{Ca}_2\text{P}_2\text{O}_7 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ ($= \text{H}_{10}\text{Ca}_{20}\text{P}_{40}\text{C}_{10}\text{O}_{195}$), and of podolite as $3\text{Ca}_2\text{P}_2\text{O}_7 \cdot \text{CaCO}_3$ ($= \text{Ca}_{10}\text{P}_{12}\text{C}_3\text{O}_{180}$).

L. J. S.

Action of Carbon Tetrachloride Vapours on Minerals and Application to Quantitative Analysis. PAUL JANNASCH (*Ber.*, 1910, 43, 3135—3136).—A claim for priority over Camboulives (this vol., ii, 202; compare Abstr., 1909, ii, 728, 767). The following analyses of a fluorapatite from Renfrew County (Ontario) are given:

| Deduct from | | | | | | | | | |
|------------------------|--------------|--------------|-------------------------|----------------------|-----------------------|----------------------|------|---------|-------|
| P_2O_5 | CaO | MgO | Fe_2O_3 | K_2O | Na_2O | H_2O | F | O for F | Total |
| 39.68 | 54.67 | 1.31 | 0.19 | 0.50 | 0.62 | 0.12 | 3.75 | -1.57 | 99.90 |
| 39.74 | 54.74 | 1.22 | 0.18 | 0.47 | 0.90 | 0.10 | 3.68 | -1.54 | 99.75 |

T. S. P.

Identity of Stelznerite with Antlerite. WALDENAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 311—312).—For the orthorhombic stelznerite from Chili, described by Arzruni and Thaddeeff (Abstr., 1893, ii, 563), the formula was given as $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$, whilst for the massive antlerite from Arizona, described by Hillebrand in 1889, the formula $3\text{CuSO}_4 \cdot 7\text{Cu}(\text{OH})_2$ was deduced. A microscopical examination of the latter shows that its optical characters, so far as these can be determined, do not differ from those of stelznerite, and it is pointed out that the analyses of antlerite approximate to the simpler formula. The name antlerite having priority, it is suggested that this should stand for the species [but how far this rule should apply in the case of incompletely described or incorrectly determined minerals is doubtful].

L. J. S.

New Kind of Vanadate in the Cupriferous Deposit of Bena d'le Padru, near Ozieri (Sassari). DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 326—333).—Analysis of the new mineral by Silvio Manis gave:

| V ₂ O ₅ | P ₂ O ₅ | PbO. | ZnO. | CuO. | Fe ₂ O ₃ | MnO. | H ₂ O. | Total. |
|-------------------------------|-------------------------------|-------|------|-------|--------------------------------|------|-------------------|--------|
| 19.87 | 0.18 | 58.76 | 2.45 | 13.13 | 6.54 | 0.05 | 3.45 | 99.43 |

Its hardness is inferior to that of calcite, and it has D₁₀₀ 5.716.

R. V. S.

Further Occurrences of Tantalum and Columbium in Western Australia. EDWARD S. SIMPSON (*Austral. Assoc. Report*, 1909, 310—315).—The following analyses are given: (I) Fergusonite from Cooglegong, D 5.82—6.65; (II) Euxenite from Cooglegong, D 5.37; (III) Microlite from Wodgina, D 5.422; (IV) Ixiolite (?) from Wodgina, D 7.36; (V) Cassiterite from Greenbushes.

| Ta ₂ O ₅ | Cb ₂ O ₅ | TiO ₂ | SnO ₂ | ThO ₂ | Y ₂ O ₃ | Er ₂ O ₃ | Ce ₂ O ₃ | $\frac{La_2O_3}{Hf_2O_3}$ | CaO. |
|--------------------------------|--------------------------------|------------------|------------------|------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------|-------|
| I. 55.51 | 2.15 | 2.20 | — | 1.02 | 23.00 | 8.38 | 0.94 | — | 2.18 |
| II. 23.10 | 4.35 | 30.43 | — | 1.76 | 15.76 | 9.27 | 1.82 | 1.73 | 1.02 |
| III. 73.54 | 3.62 | — | 0.90 | — | — | — | — | — | 13.40 |
| IV. 70.49 | 7.63 | — | 3.92 | — | — | — | — | — | 0.42 |
| V. 1.76 | — | — | 97.63 | — | — | — | — | — | — |

| FeO. | MnO. | MgO. | UO ₃ | Al ₂ O ₃ | K ₂ O. | Na ₂ O. | Ignition. | Total. |
|-----------|-------|------|-----------------|--------------------------------|-------------------|--------------------|-----------|--------|
| I. trace | 0.87 | — | 1.18 | — | — | — | 3.36 | 100.79 |
| II. trace | 0.34 | 0.35 | 6.69 | 0.76 | — | — | 2.82 | 100.20 |
| III. 3.64 | 0.60 | 0.42 | — | — | 0.20 | 1.66 | 1.23 | 99.32 |
| IV. 1.34 | 10.87 | 0.37 | — | — | — | — | 0.18 | 100.22 |
| V. 0.61 | — | — | — | — | — | — | — | 100.00 |

The analytical results for fergusonite agree with the usually accepted formula, R₂O₃Ta₂O₅; those for ixiolite, with the formula MnO₃Ta₂O₅SnO₂.

T. S. P.

Analysis of a Fossil Wood. F. HART (*Chem. Zeit.*, 1910, 34 168).—A fossil palm-tree, found in a bed of clay of Miocene age at Luxhaven on the Oste, a small tributary of the Elbe, gave:—

| | Insol. in HCl | | | | Soluble in HCl | | | | Alkalis |
|---|------------------|--------------------------------------|------------------|--------------------------------|--------------------------------|------|------|-----------------|-----------|
| Moisture, CO ₂ , H ₂ O* | SiO ₂ | (Al, Fe) ₂ O ₃ | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | and diff. |
| 14.5 | 8.21 | 51.72 | 0.26 | 0.25 | 26.50 | 2.68 | 7.04 | 0.21 | 0.23 |

* Organic matter soluble in soda was also present.

Two samples of the clay gave:

| SiO ₂ | (Al, Fe) ₂ O ₃ | CaO. | MgO. | SO ₃ | Loss on ignition. |
|------------------|--------------------------------------|------|------|-----------------|-------------------|
| 50.45 | 30.00 | 1.86 | 2.50 | 0.60 | 14.40 |
| 60.50 | 26.60 | 2.00 | 2.50 | 0.60 | 7.95 |

The ratio of silica to sesquioxides is very nearly the same in the fossil as in the first of the clay analyses (namely, 1.76 and 1.68 respectively; in the second clay analysis it is, however, 2.27); but whilst in the clay the sesquioxides are insoluble in hydrochloric acid, in the fossil they are almost wholly soluble. To explain this, it is suggested that at the time of the deposition of the clay, when this was suspended in a very finely divided state or in colloidal solution, the

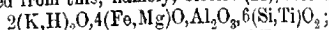
cellular organic matter of the wood exerted an adsorptive action, and resolved the clay into aluminium hydroxide and hydrated silica.

L. J. S.

Barbierite, a Monoclinic Soda-felspar. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 358—359).—Barbier and Prost (*Abstr.*, 1908, ii, 863) have recently established the existence of a monoclinic soda-felspar ($\text{NaAlSi}_3\text{O}_8$) isomorphous with orthoclase and dimorphous with albite. For this the name *barbierite* is proposed. The felspar from Kragerö with only 1.15% K_2O is nearly pure barbierite. Other analyses of soda-rich orthoclases have been given by Barbier (this vol., ii, 419).

L. J. S.

[Minerals in Dacite from Victoria.] ERNEST WILLINGTON SKEATS (*Quart. J. Geol. Soc.*, 1910, 66, 450—468).—In a description of the rocks of the Dandenong district, the following analyses, by Plante and Richards, are given of dacite (I) from Upway, and of the minerals isolated from this, namely, biotite (II), formula



hypersthene (III), formula $12(\text{Fe,Mg})\text{O}, (\text{Al,Fe})_2\text{O}_3, 16\text{SiO}_2$; ilmenite (IV), formula $(\text{Fe,Mg})\text{O}, 2\text{TiO}_2$.

| | SiO_2 | TiO_2 | Al_2O_3 | Fe_2O_3 | FeO | MnO | CaO | MgO | K_2O | Na_2O | H_2O | P_2O_5 | Total | Sp. G. |
|------|----------------|----------------|-------------------------|-------------------------|--------------|--------------|--------------|--------------|----------------------|-----------------------|----------------------|------------------------|-------|-----------------|
| I.* | 63.27 | 1.36 | 16.50 | 6.68 | 5.10 | 0.65 | 4.18 | 2.48 | 2.68 | 2.30 | 0.00 | 0.52 | 91.5 | 2.956 |
| II.* | 39.80 | 7.95 | 11.18 | 1.20 | 18.10 | 0.58 | trace | 9.88 | 6.73 | 0.35 | 0.43 | 3.20 | trace | 100.0 |
| III. | 50.42 | 3.51 | 4.06 | 2.10 | 23.74 | 0.24 | 1.30 | 13.04 | 0.09 | trace | 0.10 | 0.6 | 0.72 | 100.0 |
| IV. | — | 67.28 | — | — | 31.92 | trace | — | 0.80 | — | — | — | — | 100.0 | 4.5 |

* Also 8 (in pyrites), 0.16; Li_2O , trace.

† Also Li_2O , trace.

L. J. S.

[Minerals Associated with Diamond in Rhodesia.] FREDERIC PHILIP MENNELL (*Quart. J. Geol. Soc.*, 1910, 66, 353—375).—In a description of the geological structure of Southern Rhodesia, the following analyses, by W. C. Hancock, are given of minerals from the "blue ground" of the new Colossus diamond mine, thirty-five miles north-east of Bulawayo: I, deep red pyrope; II, small, orange coloured garnets from eclogite fragments in the "blue ground"; III, a more reddish garnet, also from eclogite; IV, deep green augite (chrome-diopside), with a pronounced parting parallel to the orthopyroxene.

| | SiO_2 | Al_2O_3 | Cr_2O_3 | Fe_2O_3 | FeO | MnO | CaO | MgO | H_2O | Total | Sp. G. |
|------|----------------|-------------------------|-------------------------|-------------------------|--------------|--------------|--------------|--------------|----------------------|--------|-----------------|
| I. | 40.43 | 19.13 | 2.12 | 4.94 | 8.66 | 0.12 | 4.44 | 20.33 | — | 100.17 | 3.71 |
| II. | 40.44 | 23.69 | 0.32 | 6.51 | 11.38 | 0.60 | 9.86 | 7.72 | — | 100.52 | 3.65 |
| III. | 39.87 | 21.47 | 0.26 | 4.95 | 8.10 | 0.23 | 12.32 | 12.89 | — | 100.09 | 3.74 |
| IV. | 53.93 | 1.90 | 0.70 | 5.07 | 2.67 | — | 13.11 | 20.03 | 1.63 | 98.99 | — |

L. J. S.

The Nature of the Pseudonepheline from Capo di Bove near Rome. FERRUCCIO ZAMBONINI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], 16, 83—86).—The pseudonepheline or pseudosommite of Capo di Bove has been re-examined. The crystallography

characters agree with those of nepheline, but the refractivity is rather higher and the double refraction lower. Analysis shows:

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | Na ₂ O | K ₂ O | Total |
|------------------|--------------------------------|--------------------------------|------|-------------------|------------------|--------|
| 33.91 | 33.04 | 2.14 | 2.55 | 12.75 | 10.06 | 100.45 |

corresponding with (Na,K)AlSiO₄, whilst nepheline always contains a higher proportion of silica. Pseudonepheline has, therefore, a composition between that of kaliophillite, KAlSiO₄, and the silicate, NaAlSiO₄, which has only been obtained artificially. C. H. D.

Physiological Chemistry.

Relative Influence of the Heat and Chemical Impurity of Close Air. LEONARD E. HILL, R. A. ROWLANDS, and H. B. WALKER. The Influence of Alcohol on the Power to Hold the Breath and Work. J. F. MACKENZIE and L. E. HILL. Compressed-air Illness. I. Solubility of Compressed Air in Water and Oil. J. F. TWORT and L. E. HILL. II. The Desaturation of the Arterial Blood as Measured by the Nitrogen Dissolved in the Urine. L. E. HILL, J. F. TWORT, and H. B. WALKER. Effect of Breathing Oxygen on the Nitrogen and Oxygen of the Urine. L. E. HILL, J. F. TWORT, H. B. WALKER, and R. A. ROWLANDS (*Proc. physiol. Soc.*, 1910, iii—iv, iv, v—vi, vi—vii, viii; *J. Physiol.*, 41).—In hot closed chambers with no ventilation the discomfort is caused by moisture rather than by chemical impurities. Half an ounce of alcohol extends the time during which a man can hold his breath while performing work. Various results showing that air is more soluble in oil than water are confirmed; fat men should be excluded from caisson work. During decompression, the nitrogen in the urine sinks; the nitrogen does not get into equilibrium with the atmospheric pressure under ten to fifteen minutes. During the breathing of oxygen the renal epithelium checks its entry into the urine; some of the dissolved nitrogen can be got out of the body by this means, but not so much as was expected. W. D. H.

A Respiration Apparatus for Isolated Organs and Small Animals. OTTO COHNHEIM. The Gaseous Metabolism of the Musculature of the Small Intestine. O. COHNHEIM and DIMITRI PLETNEFF. The Gaseous Metabolism of the Stomach Musculature. O. COHNHEIM and D. PLETNEFF. The Gaseous Metabolism of the Musculature of Stomach and Intestine during Insufficient Oxygen Supply and under the Influence of Barium Chloride. O. COHNHEIM and D. PLETNEFF (*Zeitsch. physiol. Chem.*, 1910, 69, 89—95, 96—101, 102—105, 106—107).—The apparatus described was constructed on the principle of the Atwater-Benedict machine, and was used in the experiments on stomach and

intestine which follow. The intestine of cats is treated with mercuric chloride, which destroys the cells of the mucous membrane and bacteria, but leaves the muscle in active movement in Ringer's solution. This produces 80—90 mg. of carbon dioxide per 100 grams of intestine per hour, and uses up a corresponding amount of oxygen. The gaseous metabolism is furthered if oxygen is circulated direct through the capillaries. The respiratory quotient is 0.78.

In the stomach musculature in strong activity, 170—175 mg. of carbon dioxide are produced per 100 grams per hour.

In a previous research on intestinal muscle (Abstr., 1908, ii, 209) a smaller figure was given. This is due to insufficient oxygen supply, and not to the use of barium chloride in the experiments, for that salt does not affect the amount of carbon dioxide produced.

No reference is made to the work of Brodie and others on gaseous metabolism of the small intestine during rest and activity (this vol., ii, 518). The figures there given are in terms of c.c. per gram per minute. Cohnheim's figures for the intestine muscle (85 mg. of carbon dioxide per 100 grams per hour) may be reduced to the same terms and compared with Brodie's:

| | |
|---|-----------------------------|
| c.c. of carbon dioxide in intestinal muscle : | 0.0071 (Cohnheim). |
| " " " " whole small intestine at rest : | 0.02 (Brodie) |
| " " " " epithelial cells of small intestine : | 0.0318 (Brodie's estimate). |

Brodie's further estimate is taken as fairly accurate that the muscular coat accounts for 40%, and the mucous membrane of the small intestine for the remaining 60%. If 60% of the intestine is producing carbon dioxide at the rate estimated by Brodie, and the remaining 40% at the rate determined by Cohnheim, the whole intestinal wall will produce 0.25 c.c. of carbon dioxide per gram per minute; that is to say, a figure is obtained a little higher than that actually determined by Brodie and his colleagues. The correspondence is, however, very close, taking into account that in Cohnheim's experiments the muscle was in active movement.

The research illustrates again the low metabolism of muscle as compared with secreting epithelium. W. D. H.

Composition of the Blood-gases in Chloroform Anaesthesia. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1910, 41, 246—262).—The total gas in the blood of cats as compared to dogs is low (this vol., ii, 969); as anaesthesia deepens this is increased, and the increase is mainly due to carbon dioxide. The amount of oxygen sinks, and the blood is dark in colour; this is probably because the chloroform unites with the haemoglobin, and so prevents it combining with so much oxygen. This may explain the effect on the respiratory centre. Full analytical details are given, including the amount of chloroform in the blood. W. D. H.

The Permeability of Red Blood-corpuscles in Physiological Conditions, especially to Alkali and Alkali-earth Metals. HARTOG J. HAMBURGER and F. BUBANOVIC (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 258—270).—If a disturbance within physiological limits in

the composition of the blood is produced between the corpuscles and serum, a redistribution of the inorganic constituents takes place, both as regards anions and cations. Thus, if 0.2% sodium chloride is added to serum, sodium, magnesium and calcium enter the corpuscles, and potassium leaves them. If the serum is diluted with 10% of water, sodium enters, whereas potassium, magnesium and calcium leave the corpuscles. Calcium enters the corpuscles when the blood is shaken with 5 vols. % of carbon dioxide. The fact that the corpuscles are permeable to cations is against the current view, which is based on Grüber's work. Grüber's methods and results are criticised.

W. D. H.

Comparative Investigations on the Rotatory Properties of the Plasma and Serum of Dog's Blood under Varying Conditions. I. EMIL ABDERHALDEN and PAUL KAWOHL. II. E. ABDERHALDEN and PAUL HAHN (*Zeitsch. physiol. Chem.*, 1910, 69, 1—22, 50—56).—I. Plasma has a stronger levorotatory power than serum. Repeated bleedings lower the rotation in both fluids, but the change is not a great one. Feeding on 50—500 grams of meat causes no more change than occurs without feeding; there is no rise in the rotatory power. Some preliminary experiments on feeding with carbohydrates are also given, but no noteworthy effect is seen unless large amounts of monosaccharides are given; thus laevulose raises, and dextrose depresses, the levorotation. Hunger causes considerable variations, but nothing typical. There is no difference between the optical properties of carotid and jugular blood, but the portal blood has always a higher rotation than that from other parts.

II. Injection of dextrin into the blood stream lowers the levorotation, but the effect passes off in about twenty minutes. The lowering of rotation produced by bleeding lasts longer in fasting than in well-fed animals.

W. D. H.

The Influence of Large Quantities of Water on the Optical Properties of Blood-plasma and Serum. EMIL ABDERHALDEN and ERNST RUEHL (*Zeitsch. physiol. Chem.*, 1910, 69, 57—59).—Large quantities of water were given by the alimentary canal, and this caused a noteworthy sinking of the rotatory power of the plasma and serum; this lasts for about four hours.

W. D. H.

A Method for Drying Serum. SIGMUND FRÄNKEL and ALADAR EIFFER (*Biochem. Zeitsch.*, 1910, 28, 330—331).—Attempts by various methods of evaporation do not yield good results. A perfectly dry powder was obtained by the addition of anhydrous sodium sulphate (670 grams per litre of ox-serum).

W. D. H.

Autolysis of Normal Blood. J. C. SCHIFFERS (*Biochem. Zeitsch.*, 1910, 28, 418—426).—Defibrinated blood undergoes autolysis, which is accelerated by acetic acid; proteoses, leucine, and tyrosine were found in the autolysed fluid. The active agent is destroyed by heat. The change is believed, however, to be, in part, due to a spontaneous cleavage of the protein molecule. Blood-serum shows no autolysis, but the red corpuscles do.

W. D. H.

Hæmolysis. II. Hæmolysis by Sodium Carbonate. OSKAR GROS (*Arch. exp. Path. Pharm.*, 1910, 63, 341—346. Compare this vol., ii, 51).—Hæmolysis produced by sodium carbonate runs on the same lines as that caused by ammonia. Within definite limits of concentration, the time of induction is inversely proportional to the concentration of the salt, and proportional to the amount of blood.
W. D. H.

The Hydrochloric Acid of the Gastric Juice of the Selachian Fishes. ERNST WEINLAND [with A. GROHMANN and TH. STEFFEN] (*Zeitsch. Biol.*, 1910, 55, 58—69).—The method of Sjöqvist for estimating hydrochloric acid is not practicable in the presence of chlorides of the alkali earths. Hydrochloric acid is found even though none be present in the free state if an organic acid is present also. The gastric juice of the dog fish and other selachians contains little or no free hydrochloric acid. Statements to the contrary are due to the non-recognition of the two facts mentioned above.
W. D. H.

Variations in Quantity and Composition of the Pancreatic Juices during Secretions Provoked by Secretin. S. LAJOG (Compt. rend., 1910, 151, 824—827).—Repeated injection of secretin into dogs enables a regular supply of the pancreatic fluid to be obtained during several hours. The alkalinity and diastatic activity of the juice thus obtained gradually diminishes, however, the variation in lipolytic power being more marked than the diminution in tryptic or amylolytic activity.
W. O. W.

Physiology of Digestion. II. Total Chlorine of the Animal Body. RUDOLF ROSEMANN (*Pflüger's Archiv*, 1910, 135, 177—193. Compare Abstr., 1907, ii, 706).—The author's previous work on the hydrochloric acid of the gastric juice led to the present research. The methods used and results obtained by previous workers are summarised. The fetus is richer in chlorine than the new-born animal, and the percentage amount diminishes still more after birth. The author's values for the fully-grown dog average 0.12% of chlorine. In the cat and mouse, the figure is a little higher.
W. D. H.

Metabolism Experiments as Statistical Problems. H. L. RIETZ and H. H. MITCHELL (*J. Biol. Chem.*, 1910, 8, 297—326).—Metabolism experiments should be studied mathematically, as observations on heredity are, in order to exclude the deviations which occur in physiological processes, and take place although surrounding conditions are made as constant as possible.
W. D. H.

Metabolism of Development. II. Nitrogen Balance during Pregnancy and Menstruation in the Dog. JOHN R. MURRAY (*Amer. J. Physiol.*, 1910, 27, 177—205. Compare this vol., ii, 729).—Menstruation causes a retention of nitrogen, which is to be regarded, in part, as a compensation for the blood lost. The first half of normal pregnancy is characterised by a loss of nitrogen from the mother's body. This is probably due to the action of proteolytic enzymes

produced by the embryo and not yet limited by the placenta in their action to the maternal blood. Nitrogen retention occurs in the last half of the pregnancy.

W. D. H.

The Importance of the Mechanical Part of the Work of Digestion in Relation to Metabolism in the Ox. KARL DAHM (*Biochem. Zeitsch.*, 1910, 28, 456—503).—A very important contribution to the much discussed question as to whether the work of the digestive organs is an important factor in metabolism, as Zuntz maintains, or not. A number of oxen were fed on different diets, and their metabolism and heat production determined by examining faeces, urine, and gaseous interchanges. The results confirm Zuntz's views.

W. D. H.

Digestion of Cellulose in Dogs, and the Methods for Estimating Cellulose. HANS LOHRISCH (*Zeitsch. physiol. Chem.*, 1910, 69, 143—151).—The author's previous conclusion that dogs are able to digest cellulose, he finds on further work to be incorrect. Dogs do not digest cellulose. He still holds, however, that cellulose is digestible to some extent by man in spite of the criticisms of Scheunert. The Simon-Lohrlich method for the estimation of cellulose is regarded as the best.

W. D. H.

The Work of Digestion after Carbohydrate Food, and its Dependence on the Physical Condition of the Nourishment. OTTO MÜLLER (*Biochem. Zeitsch.*, 1910, 28, 427—455).—Investigations on the gaseous metabolism of dogs show that this is much more increased by giving starch than by giving an equivalent amount of dextrose; the effect is also more prolonged after starch feeding. Older investigations on the question, in which the gaseous interchanges were not examined, are criticised. The original paper must be consulted for full analytical details and methods for calculating results; the main conclusion is that in starch feeding, for every 100 calories of the starch digested, 9.23 calories are produced over and above the nanition figure; for dextrose the figure is only 5.61. When the carbohydrates are given in small quantities, the difference is not noticeable. The low respiratory quotient found is due to the fact that the animals had fasted for two days before the experiment, therefore much of the carbohydrate given would be stored as glycogen, and fat used for combustion.

W. D. H.

Carbohydrate Metabolism in *Carcinas mænas*. E. GRAF VON SCHÖNBORN (*Zeitsch. Biol.*, 1910, 55, 70—82).—In the crabs investigated, glycogen is found in important amounts; after twenty-five days' nanition, it does not wholly disappear; its amount diminishes at first rapidly, then slowly. On then feeding upon fish, or injecting dextrose, it is again laid on until its amount may reach 2.7% of the body-weight. In the period of chitin formation in the shell, the amount of glycogen is lessened.

W. D. H.

The Influence of Carbohydrate and Fat on Protein Metabolism. II. The Effect of Phloridzin Glycosuria. E. PROVAN CATHCART and M. ROSS TAYLOR (*J. Physiol.*, 1910, 41, 276—284).—In phloridzin glycosuria, if the carbohydrate in the food is insufficient, there is no excretion of creatine. The carbohydrate cannot be replaced by fat. The output of creatine persists only as long as the glycosuria lasts. There is no apparent causal relationship between acidosis and excretion of creatine. The experiments were made on dogs. W. D. H.

Parenteral Administration of Protein. KORNÉL VON KÖRÖS (*Zeitsch. physiol. Chem.*, 1910, 69, 313—326).—If a foreign protein is injected into the circulation, it has been held that provided circulation through the alimentary canal is prevented, it passes like a foreign substance into the urine. This is not the case, proteins and proteoses pass into the urine in minimal amounts only, even though the stomach and intestine are extirpated. The injected protein remains therefore in the organism, but whether it is built into the tissues as is protein given enterally is as yet an open question. W. D. H.

Metabolism Experiments with Elastin. EMIL ADDEHOLDEN and ERNST RUEHL (*Zeitsch. physiol. Chem.*, 1910, 69, 301—309).—Elastin contains glycine in abundance, leucine, and very little glutamic acid; histidine has been found in so-called hemi-elastin, but tryptophan is absent. In the present research on dogs, elastin was prepared from the neck ligament of the ox; on artificial gastric digestion, hemi-elastin was obtained, but tryptophan was present, although whether this was due to impurities is doubtful. It is badly absorbed, the faeces containing a high percentage of nitrogen; the animals lost weight, and elastin is regarded as inferior to other proteins, although it “spares” them to some extent. It is superior to gelatin. After feeding on elastin, Borchardt (*Abstr.*, 1908, ii, 957) stated that hemi-elastin was discoverable in the blood and urine; these experiments were repeated with a wholly negative result. W. D. H.

The Assimilation of Natural and Artificial Nourishment. II. ARNOLD ORGLER (*Biochem. Zeitsch.*, 1910, 28, 359—373).—Puppies of the same litter were fed, some on cow's milk, and some on their mother's milk. They were killed and analysed, some at four and some at six weeks of age. Those fed in the natural way grew more rapidly in weight and strength than the others, and their bodies contained more fat, nitrogen, ash, and calcium. The puppies fed on cow's milk took it freely, and were found with enlarged stomachs after death. The putting on of fat per kilo. of body-weight was more rapid than in those artificially fed. If the figures are reckoned on the fat-free body, the naturally-fed animals show a higher percentage of dry residue, but the nitrogen, ash, and calcium are about equal in the two sets of animals. Dog's milk is richer than cow's milk in protein and ash, and is of greater calorific value. Analytical details are given in full, and compared with those of previous workers. W. D. H.

Distribution of Fluorine in the Human Organs. EMIL ZDAREK (*Zeitsch. physiol. Chem.*, 1910, 69, 127—137).—Fluorine is widespread in the organs; the quantity is always small, and is relatively greatest in liver, kidneys, and bone. Analyses are given in full. W. D. H.

Detection of Phosphates [in Tissues] with the Molybdate Reagent. RAPHAEL ED. LIESEGANG (*Chem. Zeit.*, 1910, 34, 1158).—Experiments showing that for histological purposes the application of the ammonium molybdate-nitric acid reagent does not localise the phosphates in tissues. L. DE K.

Incineration of Microtome Sections. RAPHAEL ED. LIESEGANG (*Biochem. Zeitsch.*, 1910, 28, 413—417).—An attempt was made in the direction of localising the occurrence of certain elements in microscopic section by incinerating them. In the early stages of heating, the blackening indicates the position of carbonaceous material, and here, as also in the later stages of complete incineration, it is still possible to identify the tissue elements, especially in thin sections. Attempts thus to localise iron microchemically were not successful, as the iron is again "masked" as oxide. A similar failure attended attempts to localise iodine in the thyroid, and the various reactions for the detection of phosphorus are either not sufficiently characteristic or worthless. W. D. H.

The Aldehydase in Animal Tissues. FR. BATELLI and LINA STERN (*Biochem. Zeitsch.*, 1910, 29, 130—151).—By aldehydase is meant the ferment which can convert an aldehyde into a mixture of the corresponding alcohol and acid. In the absence of oxygen the activity can be measured by estimating the amount of acid produced. In the presence of oxygen, certain aldehydes are oxidised further to the acid, although in many tissues the amount of alcohol-oxydase is very small. Acetaldehyde is changed in most tissues more rapidly than salicylaldehyde. Calf's spleen is an exception in this respect. Formaldehyde does not readily undergo the change. The aldehydase is contained in most tissues, especially in the liver of the horse. Preparations containing aldehydase can be produced by precipitation of the tissues by acetone. The ferment acts best in slightly alkaline medium, the optimum temperature being 60°. The rate of reaction was also studied. S. B. S.

Lipoids of the Brain. II. A New Method for the Preparation of the Galactosides and of Sphingomyelin. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1910, 1—11; *J. Physiol.*, 41. Compare Abstr., 1909, i, 282).—Cholesterol is first removed by extraction with cold acetone, and then lecithin and kephalin by extraction with ether or light petroleum; the residue is then reduced to a fine powder, and extracted with cold pyridine; the extract is reddish in colour, and shows an absorption spectrum similar to that of hæmochromogen; it is poured into acetone, and a hunky precipitate of impure galactosides (phrenosin and kersin) is thus

obtained; these can be separated by fractional crystallisation from 85% alcohol at 30° and 0°, and subsequently purified by several methods. If the residue is now extracted with warm pyridine (40—45°), sphingomyelin is dissolved out, which is precipitated by cooling to room temperature, and subsequently purified. Molisch's reaction is a very delicate one for the detection of the galactosides.

W. D. H.

Lipoids. XIII. Composition of the Spinal Cord. SIEMUND FRÄNKEL and LUDWIG DIMITZ (*Biochem. Zeitsch.*, 1910, 28, 295—319).—The spinal cord contains 74% of water, 18% of lipoids (being the part of the central nervous system richest in these substances), and 8% of the proteins described by Halliburton, who, however, put the percentage higher. The amount of water increases with age. The cholesterol present (4%) is in the free condition, as in the brain. A great part of the unsaturated phosphatides consists of cephalin; the saturated lipoids are only present to the extent of 1.5%.

W. D. H.

Union of Certain Poisons with Cardiac Muscle. HORACE M. VERNON (*J. Physiol.*, 1910, 41, 194—232).—Alcohol added to Ringer's fluid perfused through the tortoise heart lessens the amplitude of the heart's contraction; after about twelve minutes, the amplitude remains at a small, but constant, level; this effect is removed by perfusing with pure Ringer's solution. Ether and chloroform act in the same way, but smaller doses are required to produce the same effect as alcohol; their action is also reversible; the concentration of the poison does not affect this result. Hydrocyanic acid acts in the same way, except that the effect is not proportional to the concentration; greater concentrations than 0.01% permanently injure the heart. Probably the same amount of poison is united to the cardiac substance in spite of variations in its concentration. Sodium fluoride acts somewhat in the same way; on washing out with pure saline, the ventricle usually shows one to three huge waves of tonus oscillation. Formaldehyde very slowly reduces the contractions to a constant level, proportional to the concentration (0.001 to 0.008%), and recovery on washing out is very slow. Alcohol, ether, and chloroform slow, and may stop, the heart. Formaldehyde, hydrocyanic acid, and sodium fluoride seldom stopped the heart absolutely, and in many experiments did not affect its rate. Hearts depressed in vitality are more sensitive to the action of poisons, especially of chloroform. It is regarded as probable that alcohol, ether, and chloroform enter into a loose union with the colloidal lipoids or other constituents of the cardiac tissue by means of molecular valencies, whilst hydrogen cyanide, sodium fluoride, and formaldehyde enter into definite chemical combination by means of atomic valencies.

W. D. H.

Autolysis. WALTHER LINDEMANN (*Zeitsch. Biol.*, 1910, 55, 36—52).—Autolysis in the livers of rabbits, cats, and dogs was studied under aseptic conditions. Protein hydrolysis, acid formation, and development of gas occur only if the organs are kept at 37°.

Carbon dioxide and hydrogen appear in most variable proportions; hydrogen may be absent in the case of the rabbit. No constant relation-ship was found between the production of carbon dioxide and volatile fatty acids; this is against a fatty acid fermentation of carbohydrate. The possibility of the acids arising from protein was shown by the occurrence of de-amidation.

W. D. H.

The Behaviour of the Fat of Organs in Autolysis, and on Preservation Under Aseptic Conditions. KOHSHI OHTA (*Biochem. Zeitsch.*, 1910, 29, 1—12).—To investigate the question as to whether fat can be formed from proteins, liver and heart muscular tissues were preserved in the cold and at 37—40° with chloroform water, and the amounts of fatty acids in the unchanged tissues, together with the cholesterol in the changed and unchanged tissues, were estimated. It was found that there was no increase of fatty acid produced under any conditions in the liver tissue, whereas the results in the heart muscular tissue were irregular, probably owing to the want of homogeneity in the original tissue. Owing to the small quantities of cholesterol, and the consequent uncertainties due to experimental error, no conclusion could be drawn as to whether this substance increases in amount or not.

S. B. S.

The Oxidation Processes of Lipoids of the Spinal Column. E. SIGNORELLI (*Biochem. Zeitsch.*, 1910, 29, 25—30).—It has already been shown by Scaffidi that the nervous tissue, especially during degeneration, absorbs relatively large amounts of oxygen. The author now shows that the lipoids prepared from fresh nervous tissue also absorb oxygen, owing probably to the presence of unsaturated lipoids. The experiments were carried out by means of a microspirometer.

S. B. S.

The Amount of Erepsin in Blood-free Organs. OTTO CORNHIEIM and DIMITRI PLETNEFF (*Zeitsch. physiol. Chem.*, 1910, 69, 108—112).—Vernon found the duodenal mucous membrane to be richest in a peptolytic enzyme (erepsin), whilst among the organs, the kidneys possessed most and the blood least. He determined this colorimetrically by the biuret test. Abderhalden uses the splitting off of tyrosine from glycyl-tyrosine as his test for such enzymes. In the present research a slight modification of Vernon's method was employed to test the presence of erepsin in cat's organs (kidneys, lungs, muscles); the results confirm those of Vernon; the organs were freed from blood by Ringer's solution. Erepsin, or, at any rate, a peptolytic enzyme, is therefore present in the tissue cells independently of the blood.

W. D. H.

The Isolated Kidney. The Influence of Pulse Pressure upon Renal Function. DONALD R. HOOKER (*Amer. J. Physiol.*, 1910, 27, 24—44).—A perfusion apparatus for the dog's kidney is described, which yields a pulsatile wave of pressure similar to the normal pulse. The amount of urinary filtrate and the rate of blood flow vary directly as the magnitude of the pulse pressure; the amount of

protein varies inversely as this magnitude; in all cases the mean perfusion pressure was constant.

W. D. H.

The Cortex of the Suprarenal Body. K. KAWASHIMA (*Biochem. Zeitsch.*, 1910, 28, 332—339).—Extracts of the cortical region of the horse's suprarenal contain no enzyme capable of destroying adrenaline. Small quantities of adrenaline or a related substance are present.

W. D. H.

The Behaviour of the Chromaffine Substance of the Suprarenal Body in Hunger and Under the Influence of Potassium Iodide. F. VENULET and G. DMITROWSKY (*Arch. exp. Path. Pharm.*, 1910, 63, 460—464).—In inanition, the chromaffine substance of the suprarenal is diminished; administration of adrenaline under these conditions prolongs life. Potassium iodide is inhibitory towards the secretion of adrenaline, and this in addition to its depressor action is considered to explain its therapeutic use in arteriosclerosis.

W. D. H.

The Peptide-splitting Enzyme of Ovaries. A. KOBLENCZ and WALTHER LÖB (*Biochem. Zeitsch.*, 1910, 29, 102—103).—The ovaries of rabbits and pigs contain an enzyme capable of hydrolysing glycyl-tryptophan.

S. B. S.

Changes in the Skin following the Application of Local Anæsthetics. I. Ethyl Chloride. SHEPHERD IVORY FRANZ and WILLIAM C. RUEDIGER (*Amer. J. Physiol.*, 1910, 27, 45—59).—Ethyl chloride is an anæsthetic and analgesic; analgesia (insensibility to pain) being the more persistent. This is in favour of the view that pain is a sensation subserved by nerve- and end-organs distinct from those concerned in tactile impressions. Sensations of temperature are dulled.

W. D. H.

Laxatives and the Calcium of the Intestine. RICHARD CHIARI (*Arch. exp. Path. Pharm.*, 1910, 63, 434—440).—Saline purgatives which precipitate calcium ions increase the calcium in the intestinal wall, and calomel and alkaloids lessen it.

W. D. H.

Is the Stoppage of Rhythmic Contractions in a Solution of Pure Sodium Chloride Due to Increased Rate of Oxidation? JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1910, 28, 350—352).—Direct measurements show that there is no increased absorption of oxygen due to the presence of sodium chloride in solutions containing organisms which undergo rhythmic contractions, so that the question in the title is answered in the negative. The retarding action of sodium chloride on the rhythmic contractions of *Medusa* is not removed by addition of sodium cyanide.

G. S.

Production of Light by the Firefly. JOSEPH H. KASTLE and F. ALEX. McDERMOTT (*Amer. J. Physiol.*, 1910, 27, 122—151).—Three things are concerned in the production of light by living organisms: the

photogenic substance, water, and oxygen. The first is characterised by extreme irritability, but its composition is unknown. Chemical stimuli, especially ether, chloroform, carbon disulphide, carbon tetrachloride, nitrobenzene, and nitrites of certain metals, cause a continuous formation of light in the firefly, whereas normally light emission is intermittent, resembling a series of luminous explosions. Of the substances tried, sulphur dioxide is the most toxic. Great diminution of atmospheric pressure causes emission of light in the living animal and in the detached luminous organ. The photogenic material can be dried in a vacuum, and retains its power to emit light when moistened for at least thirteen months. W. D. H.

The Secretion of the Infundibular Lobe of the Pituitary Body and its Presence in Cerebrospinal Fluid. HARVEY CUSHING and EMIL GOETSCH (*Amer. J. Physiol.*, 1910, 27, 60—86).—The view that the active principle of this gland is secreted into the ventricular cavity is supported by the discovery that the cerebrospinal fluid contains a substance which acts on blood-pressure like "pituin." This can be demonstrated in concentrated specimens of the fluid. Pituin is believed to be a product of the hyaline substance of the *pars nervosa*. W. D. H.

The Reducing Properties of Milk, Liver, and Yeast. LEOPOLD ROSENTHALER (*Zeitsch. Nahr. Genussm.*, 1910, 20, 448—453).—From the results of experiments in which the action of milk on phenylglyoxylic acid was investigated, the author comes to the conclusion that the reducing power of milk on such substances as the methylene-blue of Schardinger's reagent (*Abstr.*, 1903, ii, 190), etc., is due to bacterial action, and not to that of enzymes. The analogous actions of liver and yeast are due to the same cause. W. P. S.

Aporrhagma. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, 69, 265—272).—The name aporrhagma is given to the decomposition products of protein amino-acids formed by physiological processes in the living plant or animal, and includes the common ptomaines and acids formed by putrefaction.

Attention is drawn to the fact that although methylated nitrogenous compounds are present in large quantities in vegetable tissues, they are rarely met with in animal tissues. Methylated glycine has been extracted from the muscles of *Crangon vulgaris*, *Astacus fluviatilis*, and *Acanthias vulgaris*, but does not appear to be present in the muscle of mammals. It is suggested that in warm-blooded animals the nitrogenous products are got rid of by processes of oxidation, but that in plants and cold-blooded animals they are removed by means of complete methylation. Methylation can occur in the case of warm-blooded animals when oxidation is stopped to an appreciable extent, for example, in cases of phosphorus poisoning.

A list of aporrhagma and their corresponding amino-acids is given, and also a list of methylated aporrhagma. J. J. S.

A New Aporrhagma Prepared by Bacterial Agencies. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1910, 69, 273—281. Compare this vol., i, 419).—Lysine mixed with Witte's peptone and dextrose

undergoes bacterial putrefaction in the presence of a small amount of putrefying pancreas, and, after nineteen days at 36° , yields appreciable amounts of pentamethylenediamine, which can be isolated as the picrate or aurichloride. A small amount of a product which yields a readily soluble platinichloride is also formed.

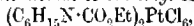
Arginine under similar conditions yields tetramethylenediamine and δ -aminovaleric acid, but not agmatine, and glutamic acid yields γ -amino-butyric acid (compare Schotten, Abstr., 1883, 813; Gabriel, *ibid.*, 1896, 360), by the elimination of carbon dioxide.

It has not been found possible to isolate methylamine* and ethylamine from the products formed by the action of anaerobic bacteria on glycine and alanine.

J. J. S.

A Methylated Aporrhagma from Animal Tissues. R. ENGELAND and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, 69, 282—285).—The γ -aminobutyric acid obtained from glutamic acid (compare Ackermann, preceding abstract) is identical with the synthetical acid. The aurichloride, $C_4H_9O_2N, HAuCl_4$, crystallises in glistening plates, m. p. 138° .

When methylated, the γ -amino-acid yields a product from which an aurichloride, $C_7H_{16}O_2N, HAuCl_4$, can be obtained, identical with the aurichloride, m. p. 203° , from γ -butyrobetaine chloride isolated by Takeda (this vol., ii, 797) from the urine of dogs poisoned by phosphorus. The platinichloride of the ethyl ester,



has m. p. 222° (decomp.). The occurrence of this betaine in substances of animal origin is due to the decomposition of glutamic acid and the methylation of the γ -aminobutyric acid. The α -hydroxy- γ -butyrobetaine formed in muscle extract is probably the first oxidation product of γ -butyrobetaine.

J. J. S.

Distribution of Nitrogen in the Intestinal Excreta. HENRI LABBÉ (*Compt. rend.*, 1910, 151, 822—824).—Normal human faeces were extracted successively with ether, benzene, aqueous sodium carbonate, and glacial acetic acid. Nitrogen was determined in the original faeces, in each extract, and in the insoluble residue. The results are given in tabular form. The benzene extract appeared to contain the substances of the lecithin type, whilst the alkaline extract probably contained the amino-acids.

W. O. W.

The Secretion of Urine. JOSEPH BARCROFT and HERMAN STRAUB (*J. Physiol.*, 1910, 41, 145—167).—The diuretics studied fall into two groups: (1) those which produce urine without alteration in the gaseous exchange of the kidney (Ringer's solution, and sodium chloride in hyper- and hypo-tonic solutions); (2) those which cause increased gaseous exchange (urea, caffeine, sodium sulphate, phloridzin). In the case of urea and caffeine there is a definite poisoning action, as shown by subsequent depression of the gaseous exchange. The distinctive features of the urine produced by the second class are attained by a process of secretion on the part of the tubules, and not by a process of re-absorption. After poisoning the cells by corrosive

sublimate or by the diuretics of the second class, a flow of urine can still be produced by the first class of diuretics; the urine so produced appears to be isotonic with the blood-serum. Clamping the kidney vessels for fifteen minutes after washing out with Ringer's solution does not abolish its power of secretion. The special interest of the research is the action of diuretics of the first class, and those produce urine independently of secretory activity (as judged by the absence of increased metabolism), and so their action must be attributed to mechanical filtration; the experimental methods adopted were such that changes in rate of blood flow or of blood pressure could be excluded. The proteins of the blood-plasma in virtue of their osmotic pressure would attract water into the blood; the capillary pressure would drive water into the urine. Suppose, for instance, that the capillary pressure is equal to 27 mm. of mercury, and that the osmotic pressure of the proteins is a little lower, say, 25, as it probably is in normal circumstances, then the available pressure for filtration would be 2 mm. If the amount of protein in the blood-plasma were reduced to half, the osmotic pressure will be reduced to 12.5, and the available filtering pressure is thus 14.5, or seven-fold increase, and diuresis will occur. This argument was justified by testing it as follows: the animal was bled very considerably, and the blood replaced by Ringer's solution containing blood corpuscles in suspension; the diuresis so produced was very considerable, although the blood pressure was very low, and this was attended with no increase in the gaseous exchange.

W. D. H.

A Comparison of the Total Nitrogen Excretion of either Kidney in Normal Individuals. THEODORE E. BARRINGER, jun., and BENJ. S. BARRINGER (*Amer. J. Physiol.*, 1910, 27, 119—121).—Observations were made on eleven young men. One ureter was catheterised, a bladder catheter collecting the urine from the other kidney. Details are given of the quantity of urine, in periods varying from twenty to one hundred and twenty minutes, secreted by each kidney, also the total nitrogen, and the sum of urea and ammonia nitrogen. The differences noted are usually small.

W. D. H.

The Excretion of Parenterally Administered Creatine in Mammals. CORNELIS A. PEKELHARING and C. J. C. VAN HOOGENHUYZE (*Zeitsch. physiol. Chem.*, 1910, 69, 395—407).—Injection of creatine into the blood-stream of rabbits, led to the result that this substance is, in part, decomposed in the body, and partly excreted as creatinine by the kidneys. The liver appears to be specially concerned in its destruction and in its conversion into creatinine.

W. D. H.

The Excretion of Organically United Phosphorus in Urine. KURA KONDO (*Biochem. Zeitsch.*, 1910, 23, 200—207).—Previous work on the organic phosphorus compounds of the urine in health and disease have shown that they are increased by the administration of glycerol-phosphates and lecithin. In the present research, a dog was fed on horse-flesh and lard, and then to this were added for two or three days' periods, brain, casein, and thymus. On normal days the

organic phosphorus in percentage parts of total phosphorus averaged 2.7, on the brain days 3.3, and on the casein and thymus days 1.5. W. D. H.

The Influence of the Fat of the Food Ingested on the Excretion of the Acetone Substances. GUNNAR FOSSNER (*Chem. Zentr.*, 1909, ii, 1759; from *Skand. Arch. Physiol.*, 1909, 22, 349—392).—The excretion of acetone and β -hydroxybutyric acid depends on the food ingested. After meals there is a regular increase in the excretion of acetone substances, and the missing of a meal causes a distinct change in the regular curve representing the excretion, and a marked diminution in the amounts excreted. The excretion depends on the fat ingested; no difference could be detected between the action of the higher fatty acids (lard, etc.) and the lower fatty acids (hutter). When the store of glycogen in the body had diminished, relatively small quantities of fat caused acidosis, similar to that of severe diabetes. S. B. S.

The Influence of Muscular Work on the Excretion of Acetone Substances, with Diets Poor in Carbohydrates. GUNNAR FOSSNER (*Chem. Zentr.*, 1909, ii, 1760; from *Skand. Arch. Physiol.*, 1909, 22, 393—406).—On different days, certain amounts of muscular work were performed (marching), which were in the ratios of 1, 2, 3, and 4. The average diet consisted of 111.7 grams protein, 239 grams fat, and 59.4 grams carbohydrates. Muscular work was found to diminish the body reserve of carbohydrates, which are concerned in the formation of acetone substances. This diminution was, however, only proportional to the amount of work performed within certain limits. The maximal action under the condition of experiments was attained by a forced march lasting for two to thirty-six minutes. S. B. S.

Melanuria. HANS EPPINGER (*Biochem. Zeitsch.*, 1910, 28, 181—192).—The origin of the black pigment which occurs in certain malignant tumours and passes into the urine is obscure, and the suggestion that it originates from tyrosine by the action of a tyrosinase is due to experiments *in vitro* only. The present research shows that this pigment (melanin) originates from tryptophan. By feeding with tryptophan, the excretion of the pigment is increased three-fold, whereas tyrosine and phenylalanine, the parent substances of homogentisic acid, have no effect. The urine is sometimes darkly coloured when passed, sometimes the darkening comes on after exposure to the air, but in all cases of melanotic tumour, it appears on the addition of oxidising agents; the material in the urine is then not melanin, but melanogen. This can be precipitated from the urine with sulphuric acid and mercuric sulphate, and can then be dissolved out from the precipitate by a method which is described in full, and finally obtained in crystalline form. These crystals show all the colour and other reactions of melanogen as contained in the original urine. The following formula was calculated from its percentage composition: $C_6H_{12}O_4N_2S$, and it is regarded provisionally as a hydroxy- γ -methylpyrrolidinedicarboxylic acid in the form of an ethereal sulphate. Another

substance was separated from the same urine; it is probably related to the first, but this requires further investigation. W. D. H.

Acapnia and Shock. VII. Failure of the Circulation. YANDELL HENDERSON (*Amer. J. Physiol.*, 1910, 27, 152—176. Compare this vol., ii, 622).—The essential factor in the circulation in shock is not heart failure, but failure of the veno-pressor mechanism, which consists, in part, of the tonus of the tissues and, in part, of osmotic processes. Tonus is largely dependent on the carbon dioxide they contain, and when the tension of carbon dioxide (regulated by the respiratory centre) is diminished in acapnia, the blood stagnates in the venous reservoirs. Acapnia upsets osmotic processes; water passes out of the blood into the tissues, and is ultimately followed by tissue asphyxia and acidosis. W. D. H.

The Fundamental Constituents of Tumour Cells. EMIL ADDERHALDEN and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1910, 69, 66—71).—Tyrosine, glutamic acid, and glycine were estimated in the cell proteins derived from various malignant tumours. The different kinds of tumours all yielded the three amino acids in approximately the same proportion. W. D. H.

The Theory of the Wassermann Reaction. E. GATZ and R. INABA (*Biochem. Zeitsch.*, 1910, 28, 374—391).—Sachs and Rondoni have shown that dilution of the alcoholic extract of the syphilitic liver with salt solution causes a cloudiness, which varies as the dilution is effected slowly or rapidly. The manner of dilution influences the power of the extract in uniting with complement, and they explain this as due to a physical cause, namely, the size of the particles in suspension. There is an undoubted alteration as Sachs and Rondoni described, and this disappears on cooling; moreover, the difference does not run parallel to the change in hæmolytic power; the latter, however, does not remain unaltered. Sharper results are obtained in extracts diluted slowly, and those who use the Wassermann reaction for the biological detection of syphilis must recognise the importance of this factor. It appears doubtful if the explanation is wholly physical. W. D. H.

Serological Studies with the Help of the Optical Method.
XI. Parenteral Administration of Carbohydrates. EMIL ADDERHALDEN and GEORG KAPFERBERGER (*Zeitsch. physiol. Chem.*, 1910, 69, 23—49).—Sucrose injected either into the blood or subcutaneously is inverted in the blood, but great differences are seen in different animals. Lactose is also affected, but not raffinose. After the injection of lactose, dog's serum or plasma inverts sucrose and lactose, but not raffinose. The action of these fluids on the two disaccharides is noticeable seven to eight hours after a subcutaneous injection of either, and lasts at least fourteen days. Whether the urine has the same power has not yet been investigated. The agent in the blood that acts on the sugars, dialyses into distilled water. A temperature of 60° destroys the power, and of 4° lessens it. W. D. H.

The Influence of Pharmacological Agents on Oxidation in the Organism. JULIUS BAER and WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1910, 63, 441—459).—The importance of oxidation as a source of energy, and the way in which body functions are influenced by drugs acting on oxidation processes are well illustrated by recent work on narcosis. In the present research, the point investigated was acetone formation in the liver perfused with various drugs: namely, potassium cyanide, chloral hydrate, trichloroacetic acid, dimethylbarbituric acid or ethylbarbituric acid (veronal), salicylic acid, salicylaldehyde, saligenin, *p*-hydroxybenzoic acid and aldehyde, and *m*-hydroxybenzoic acid and aldehyde. All of these inhibit acetone formation in varying degrees, but the figures given show that the variation is not proportional to their effect on oxidation; indeed, some increase oxidative processes. In the oxidation of butyric and hydroxybutyric acids in the liver, two different processes or factors have therefore to be dealt with.

W. D. H.

Behaviour of Phloridzin after Extirpation of the Kidneys. ERICH LESCHKE. Answer to the Preceding. KARL GLAFSENDA and ERNST P. PICK (*Pflüger's Archiv*, 1910, 135, 171—175, 176. Compare this vol., ii, 530).—Polemical. Both sides maintain their original position.

W. D. H.

Quantitative Investigations on the Chemistry of Strophanthin Action. WALTHER STRAUB (*Biochem. Zeitsch.*, 1910, 22, 392—407).—Alkaloids which act on certain organs, such as the heart, can be washed out and re-obtained in the washings, and their action is thus reversible. This is not the case with the digitalis glucoside. Strophanthin is in this relation similar to alkaloids, and its action is largely reversible. Tested on a frog's heart by perfusion, the reaction is proportional to the concentration of the drug, and there is probably a chemical action between the cell constituents and the glucoside, although very little of the latter is used in the combination or interaction, and there is no storage in the heart muscle.

W. D. H.

The Systolic and Diastolic Heart-Action of Strophanthin. N. WERSCHNIN (*Arch. exp. Path. Pharm.*, 1910, 63, 386—404).—This drug in Ringer's solution applied to the exterior or interior of the frog's heart leads in small concentrations to diastolic stoppage, in medium doses to systolic stoppage, and in high concentrations to diastolic stoppage and paralysis. Mixed with blood-serum, the toxic power is much increased. This is, in part, due to the lipoids present, and lecithin exerts a similar action, but the effect in producing systolic stoppage appears to be specially due to the salts of the serum, particularly those of calcium, but calcium salts only exert this influence when applied endocardially.

W. D. H.

The Action of Strophanthin on the Blood-Vessels. MAX KASZTAN (*Arch. exp. Path. Pharm.*, 1910, 63, 405—423).—The effect of members of the digitalis family in raising arterial pressure is, in part, due to vaso-constriction, and large doses will soon contract the

kidney blood-vessels and lessen the flow of urine. The present research specially takes up this point, and the organs of cats, rabbits, and dogs were perfused with strophanthin in Ringer's solution. Solutions of one or more per million constrict the blood-vessels of kidney and intestine; concentrations below this dilate them, but here a difference between the kidney and intestine is noted, for smaller concentrations, which constrict the intestinal, will still dilate the kidney blood-vessels.

W. D. H.

[Physiological] Action of Atropine, Pilocarpine, and Physostigmine. ARTHUR R. CUSHNY (*J. Physiol.*, 1910, 41, 233—245).—Pilocarpine causes contraction or inhibition of the cat's uterus, according to the condition of the organ, in this resembling the effects of adrenaline or hypogastric stimulation. Its contractor action is antagonised by ergotoxine, as is that of adrenaline or electric stimulation. It differs from adrenaline in being antagonised completely by atropine whether it contracts or inhibits the uterus. Physostigmine contracts the uterus, and is antagonised by atropine. It is suggested that pilocarpine and atropine act on receptive substances associated with the nerve impulse path to the uterus, but do not lie actually on this path. Physostigmine may probably affect the receptors associated with the augmentor path only. In the case of other abdominal organs, the same explanation is regarded as tenable, whilst, in other cases, the receptive substances are regarded as lying on the impulse path, since this is interrupted by atropine.

W. D. H.

The Behaviour of Morphine in the Frog. BRONISLAW FRENKEL (*Arch. exp. Path. Pharm.*, 1910, 63, 331—340).—Most previous workers on morphine have employed warm-blooded animals. Frogs differ from these in the prolonged period of primary excitation, culminating in tetanus, and in manifesting no immunity. Morphine is retained for a long time in the frog's body; after eight days it is, however, all eliminated, mainly by the alimentary tract, from which 65% of the amount given is recoverable; comparatively little (10%) is destroyed in the body. None is found in the central nervous system, but the liver, and next to that the muscles, contain most. The destruction is increased by an elevation of body-temperature and of oxygen tension.

W. D. H.

Influence of the Concentration of Hydroxyl Ions in a Sodium Chloride Solution on the Relative Anti-Toxic Action of Potassium and Calcium. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, 28, 176—180).—The poisonous action of sodium chloride on the developing fertilised eggs of the sea-urchin is neutralised to a greater extent by potassium than by calcium in neutral or slightly acid solution; in alkaline solution, on the other hand, calcium is more effective than potassium. In all cases the effect of a mixture of potassium and calcium is greater than the sum of the separate effects. Addition of alkali to a mixture of potassium and sodium chloride increases the poisonous action, whereas alkali renders a mixture of sodium and calcium chloride less poisonous.

G. S.

Why Does Sodium Cyanide Diminish the Poisonous Action of Sodium Chloride on Sea-Urchin's Eggs? JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1910, 28, 340—349).—Warburg (this vol., ii, 628) accounts for the poisonous action of sodium chloride on sea-urchin's eggs on the assumption that it increases the oxidation processes to such an extent that the egg is disadvantageously affected, the favouring effect of the calcium being due to its property of bringing back the rate of oxidation to the normal value. The authors have determined the amount of oxygen used up when the eggs develop in different solutions, and show that in sodium chloride solution there is no increase, but if anything a decrease, in the amount of oxygen absorbed. Warburg's observation that more oxygen is used up in a given time in a solution containing sodium chloride and cyanide than in the same solution with the addition of calcium, is confirmed, but no final explanation is advanced. The anti-toxic effect of sodium cyanide in a solution containing sodium chloride is ascribed to the former substance retarding the development of the egg or the oxidation changes accompanying development. G. S.

The Inhibition of the Toxic Action of Certain Poisons on the Eggs of Sea-Urchins Due to Depression of Oxidation in the Eggs. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, 29, 80—95).—It was found that the stoppage of oxidation in the eggs, either by sodium cyanide or by driving out oxygen from the artificial sea-water by hydrogen, inhibited the toxic action of the following classes of substances: (1) Neutral salt solutions; (2) sugar solutions; (3) hyper- and hypo-tonic solutions; (4) narcotics (chloral hydrate, phenylurethane, chloroform, and alcohol). This action of deficient oxidation cannot be due to inhibition of the bifurcation process, for it inhibits the toxic action of substances like chloral hydrate, which themselves inhibit the bifurcation of the egg. S. B. S.

The Removal of the Poisonous Effects of Hydrocyanic Acid by Substances which Split off Sulphur. JOSEF HEARING (*Biochem. Zeitsch.*, 1910, 28, 208—212).—Lang found that hydrocyanic acid compounds led to the excretion of thiocyanates, and in minced organs the change of potassium cyanide into thiocyanate also occurs, the sulphur arising probably from the cystine of protein. He further showed that various sulphur compounds protect the organism against the poisonous effects of hydrocyanic acid. Reid Hunt and others have confirmed this. In the present research on rabbits, the antidotes investigated were sodium tetrathionate, cystine, β -thiolactic acid, and α - and β -dithiodilactic acids, and Lovén's trithio-compound, $C_6H_{10}O_4S_3$. All were protective in some degree, but none reach thiosulphate in efficiency. W. D. H.

The Supposed Immunity of Toads to their own Poison (Secretion of Skin Glands). HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1910, 63, 374—385).—It has been generally stated that toads, like snakes, are immune to their own poison. The cutaneous secretion

of toads contains several active constituents, namely, a hæmolysin called phrynolysin, and two substances, bufonin, similar to cholesterol, and an easily soluble substance, bufotalin. The last two substances produce the main toxic symptom, namely, a digitalis-like action on the heart. It is shown in the present research that the hearts of frogs are easily affected by the toad's poison, stoppage and systolic contracture being produced; the same occurs also in the toad's heart. This action is to a great extent annulled by previous treatment of the secretion with cholesterol.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Spontaneous Ignition of Coal. ERNST GALLE (*Centr. Bakt. Par.*, 1910, ii, 23, 461—473).—The bacteriological examination of five kinds of coal showed the presence of seven kinds of spores, of which three were identified as *Bacillus subtilis*, *B. mesentericus*, and a kind of *Narcina*. The spores develop at the ordinary temperature and without air, and non-sterilised coal, moistened with tap-water, gave in one experiment a luxuriant growth of bacteria.

Further experiments on the production of gas from coal by the action of bacteria showed that four of the seven microbes produce inflammable gas, about three-fourths methane, about one-fifth carbon dioxide, with small amounts of carbon monoxide. The bacterial action was found to result in a rise of temperature, the greatest effect being produced by *B. pseudosubtilis* (1.3°). Finally, it is shown that coal which has been subjected to the action of the bacteria ignites at a lower temperature.

The conclusion is drawn that whilst bacteria are not the direct cause of the spontaneous ignition of coal, they may play an important part in the production of conditions which result in ignition.

N. H. J. M.

The Destruction of Gelatin by Micrococcus prodigiosus. P. MESEHNITZKY (*Biochem. Zeitsch.*, 1910, 29, 101—125).—*Micrococcus prodigiosus* contains an enzyme which is capable of liquefying gelatin, and can be detected in culture media after some days. It is very heat-stable. The products of the action of the organism on gelatin were also investigated, and the amounts of nitrogenous matter precipitable by tannin solutions after varying intervals of culture were estimated. In addition to these peptides, crystalline substances were also produced, of which only glycine was identified with certainty. Probably leucine and proline were also produced.

S. B. S.

Action of Nitrates in Alcoholic Fermentation. AUGUSTE ERSBACH and A. LANZENBERG (*Compt. rend.*, 1910, 151, 726—729).—It has been held that the presence of nitrates during alcoholic ferment-

tation is harmful, owing to the toxicity of these substances towards yeast. This view, based on the experiments of Mayer (1869) and of Dubrunfaut (*Compt. rend.*, 1871, 73, 263), is now shown to be incorrect. Potassium nitrate has a slightly inhibitory effect when present to the extent of 0.1%, but in concentrations exceeding this, up to 2%, it strongly stimulates the production of alcohol.

Experiments were also conducted on zymase with similar results; the amount of carbon dioxide produced was found to increase to a marked extent when the salt was present in 0.5—4% solution. The optimum concentration varied with the nature of the yeast from which the enzyme was prepared. It was found, however, that the multiplication of yeast cells is checked by nitrates, especially in the more concentrated solutions.

W. O. W.

Influence of Nitrates on Alcoholic Ferments. E. KATSER (*Compt. rend.*, 1910, 151, 816—817. Compare Abstr., 1907, ii, 268, 383, 903; Fernbach and Lanzenberg, preceding abstract).—Manganese nitrate is even more active than the alkali nitrates in promoting alcoholic fermentation. The optimum dose of this salt varies with the nature of the yeast.

W. O. W.

Influence of Environment on Enzymic Action. FREDERICK W. PAVY and HUBERT W. BYWATERS (*J. Physiol.*, 1910, 41, 168—193).—The inverting power of an aqueous extract of yeast is increased ten to fifteen-fold by the addition of a boiled extract of yeast. This is attributed to the acidity of the boiled extract, for the same results can be obtained by substituting acetic acid for the boiled extract. If yeast cells are used, acetic acid has the same activating effect up to a certain optimum point, after which addition of acid diminishes the inverting power. After desiccation, treatment with alcohol, or grinding with kieselguhr, yeast yields an aqueous extract with enhanced enzymic power, which acid fails almost entirely to increase further. The activity produced by acid can be removed by the addition of alkali. The diastatic enzyme of the oyster is influenced by boiled oyster extract and by acetic acid in the same way, but not to so great an extent. The addition of acid, not only increases the amount of reducing substance, but also increases its reducing power. The post-mortem production of sugar in the liver can be checked by an alkaline injection, and subsequently the production of sugar can be increased by rising amounts of acid until an optimum is reached. The dried or coagulated liver behaves to acid and alkali like the fresh organ. The post-mortem production of sugar and of acid by the liver runs on parallel lines, and the acidity so produced is regarded as the governing factor for sugar formation. Fluorides restrain the formation of both acid and sugar.

W. D. H.

The Kinetics of Toxic Action of Dissolved Substances. I. The Influence of Concentration. THEODOR PAUL, GUSTAV BIRNSTEIN, and ANTON REUSS (*Biochem. Zeitsch.*, 1910, 29, 202—248).—The disinfecting action, determined by means of the Krönig-Paul garnet method, of various acids on different bacteria was estimated. Acetic

and *n*-butyric acids were found to be more powerful disinfectants than hydrochloric acid in isohydric solutions. The disinfection constant of hydrochloric acid in $N/25$ — $N/150$ solutions was found to be approximately proportional to the square-root of the concentration of the acid. For butyric acid in concentrations $N/6.6$ — $N/26$, it was proportional to the square of the concentration, or for acetic acid in concentrations $N/2$ — $N/31$, the disinfection rate was approximately proportional to the concentration itself. The relationship between the disinfecting action and concentration of a substance can be expressed by the general equation: $K = A.C^B$, where K = constant of disinfection rate, C = concentration, and A and B are constants. The exponent B is the characteristic constant for any particular disinfectant. S. B. S.

The Kinetics of Toxic Action of Dissolved Substances. II. The Influence of Neutral Salts and Temperature on the Disinfection Rate of Acids. THEODOR PAUL, GUSTAV BIRSTEIN, and ANTON REUSS (*Biochem. Zeitsch.*, 1910, 29, 249—278).—Certain inorganic substances increase the disinfection rate of inorganic acids without themselves acting as disinfectants; an aqueous solution with equivalent quantities of the acid HX , and the salt MX , has approximately the same disinfection rate as an acid HX . The disinfection rates of acid-salt mixtures with different contents in salt are approximately the same as those of the salts having the corresponding concentration. The temperature-coefficients of the disinfection rates were also determined. S. B. S.

Catalase of Moulds. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1910, 32, 1357—1361).—A study of various species of *Penicillium* and *Aspergillus* has shown that these moulds contain catalase. When the mycelium first appears on the surface of the culture-medium, it contains a very active catalase, but, after about fifteen days, the quantity of this enzyme in the cells of the fungus gradually decreases, whilst that in the medium steadily increases. The means by which this passage of the catalase from the mould into the medium is effected cannot at present be explained, but it seems probable that some of the cells of the fungus undergo disintegration or suffer a loss of vitality, thus allowing the enzyme to diffuse or to be mechanically discharged into the medium. E. G.

Formation of Hydrogen Cyanide in the Germination of Seeds. CIRO RAVENNA and M. ZAMORANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 356—361).—Although the seeds of *Sorghum vulgare* do not contain hydrogen cyanide, yet the distillate from them when germinating always yields that substance. This is the case whether germination takes place in the dark or in light, and the amount found increases to a certain limit (0.08% of the weight of the seeds), then decreases. The seeds of *Linum usitatissimum*, which contain hydrogen cyanide (0.027%), behave similarly, but the maximum amount is greater (0.5%). It is suggested that carbon dioxide or carbohydrates are concerned in the formation of the acid. Less was produced (in some experiments) in the absence of carbon dioxide,

whilst seedlings grown in the dark and supplied with dextrose produced more than similar etiolated plants not so treated.

R. V. S.

The Elective Rôle of the Root in the Absorption of Salts. JEAN DE RUFZ DE LAVISON (*Compt. rend.*, 1910, 151, 675—677).—The rate of absorption of sodium, potassium, and calcium chloride from aqueous solutions by the cut stems and roots of plants has been determined. It was found in the case of the haricot that sodium chloride was not absorbed by the roots, whilst considerable quantities passed into the stem. The latter absorbed all the salts presented to it with equal facility, whilst the roots showed a marked selective action.

W. O. W.

Cryoscopic Determination of the Osmotic Pressures of Some Plant Organs. W. R. GELSTON ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1910, 12, 463—469).—Records are given of measurements of the osmotic pressure of the juices extracted from over fifty fruits, leaves, stems, etc., of plants. In the case of fruits the pressures varied from 5.94 atm. for a specimen of *Lycopersicon esculentum* to 28.27 to 29.53 atm. for *Prunus communis*, the high numbers in the latter case being due probably to the sugars. *Citrus Limonum* gives larger variations, 10.46 to 12.21 atm. for samples obtained in August, and 12.05 to 14.06 atm. for those obtained in February. The pressure in the rind is somewhat lower. The red stems of *Rheum officinale* gave 6.52 atm., this low number being associated with the relatively low molecular weight of oxalic acid, the chief constituent of the juice.

The pressure in the underground organs studied ranged from 6.5 atm. in the tubers of *Solanum tuberosum* to 18.7 atm. in the tubers of *Helianthus tuberosus*.

Calculations of the mean molecular weight showed that the red stem of *Rheum officinale* gave the lowest value, 76, and the tubers of *Helianthus tuberosus* the highest value, 394. The fruits gave values varying from 110 to 231.

The author concludes that similar plant organs of the same species have approximately equal osmotic pressures, but this deduction does not apply to leaves.

E. J. R.

Hydrocarbons of Vegetable Origin. TIMOTHÉE KLOBB, JULES GARNIER, and R. EHRWEIN (*Bull. Soc. chim.*, 1910, [iv], 7, 940—950). Compare Klobb and Fandre, *Abstr.*, 1907, ii, 123).—Methods for the isolation of hydrocarbons occurring in plants are described, and a number of the hydrocarbons are characterised. Many similar saturated hydrocarbons of vegetable origin have been described by Power and his collaborators.

The plant material, usually flowers, is extracted with either cold or warm light petroleum, and the soft extract left on removal of most of the solvent is dissolved as far as possible in boiling acetone. From the filtered hot acetone solution the hydrocarbon separates on cooling, and may be purified if necessary by boiling with potassium hydroxide

in alcohol and subsequent recrystallisation from ether or acetone. An alternative process consists in treating a concentrated alcoholic extract of the flowers with aqueous ammonia solution (15–20%) for several days to remove tannins, etc., and then extracting with ether. The residue left on distilling off the ether is treated with potassium hydroxide in alcohol, the solvent distilled off, and the residue poured into water and extracted with ether. The residue from the last solvent is extracted with boiling alcohol, which, on cooling, deposits the hydrocarbon in crystalline form. These hydrocarbons dissolve in warm light petroleum, chloroform, or carbon disulphide, and can be obtained in microscopic crystals from boiling acetone or alcohol, but they assume a more definitely crystalline form if left in contact with acetone during one or two days, or if obtained by slow evaporation from dilute solutions in ether. The melting point varies from 53° to 65° (Maqacune block). They are unaffected by bromine or potassium permanganate.

The flowers of *Arnica montana* yield, in addition to arnidiol (Abstr., 1904, i, 410; 1905, i, 594), a mixture of hydrocarbons, from which one having the formula $C_{30}H_{62}$, m. p. 62°, has been isolated in a pure state (compare Börner, *Inaug. Diss.*, Erlangen, 1892). *Matricaria chamomilla* flowers, treated by the second general process, furnish a hydrocarbon, $C_{29}H_{60}$, m. p. 52–54°, which crystallises in colourless lamellae. The hydrocarbon, $C_{25}H_{50}$, from *Antennaria dioica*, m. p. 64–66°, crystallises in nacreous lamellae from acetone. Worm seeds (flowers of *Artemisia maritima*) yield a hydrocarbon, $C_{32}H_{66}$, m. p. 55–58°, which crystallises in colourless lamellae, and even after purification evolves hydrogen bromide with bromine in carbon tetrachloride. The hydrocarbon, $C_{27}H_{56}$, from *Fussilago fufura* flowers, m. p. 57–59°, forms nacreous, hexagonal lamellae. The flowers of *Tilia europaea* yield a hydrocarbon, $C_{28}H_{58}$, m. p. 54–56°. The hydrocarbon isolated by Naudin from chamomile flowers (Abstr., 1884, 391) is shown to have the formula $C_{30}H_{62}$; it melts at 64°, and crystallises slowly from ether in colourless lamellae.

The formulae assigned to the various hydrocarbons have been controlled in most cases by cryoscopic determinations in naphthalene.

T. A. II.

Formation and Distribution of Certain Alkaloids in *Papaver somniferum*. M. KERDOSCH (*Pharm. Weekblad*, 1910, 47, 1062–1074, 1081–1094, 1106–1119).—An investigation of the formation and distribution of the alkaloids of *Papaver somniferum* in the different parts of the plant at various stages of its growth. The seed contains a trace of narcotine and amorphous alkaloids. After three days' germination, the seeds have developed an appreciable quantity of narcotine, and the alkaloids make their appearance in the plant in the order: narcotine, codeine, morphine, papaverine, narcaine, and thebaine. When the plants are 5–7 cm. high they contain the four alkaloids first named, and they are present in all the organs of the plant from the time of flowering until it reaches maturity, when all the organs contain narcotine, codeine, and morphine. The composition of the sap differs in different parts of the plant. Germina-

tion of the seeds in an atmosphere free from nitrogen also produces narcotine, its formation being occasioned by the decomposition of proteins. The proportion of narcotine in the buds is much greater than in the unripe seed husks.

With a solution of cadmium iodide (1.8 gram) and caesium iodide (5 gram) in 100 c.c. of water, papaverine, codeine and morphine yield additive products readily identified by their crystalline form. On addition of the reagent, each of the six alkaloids gives an amorphous precipitate; on warming, the additive products of those named dissolve, and crystallise on cooling, whilst those of the others remain amorphous.

A. J. W.

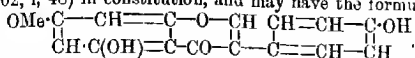
Chemical Examination of the Bark of a Species of *Prunus*. HORACE FINNEMORE (*Pharm. Journ.*, 1910, [iv], 31, 604—607).—A spurious substitute for *Prunus serotina* bark, which is very similar to the bark of *P. emarginata*, has been examined and found to differ from the true bark in containing no cyanogenetic glucoside yielding benzaldehyde on hydrolysis (Power and Moore, *Trans.*, 1909, 95, 243). It contains quercimeritrin (Perkin, *Trans.*, 1909, 95, 2181), a new colouring matter glucoside (prunitrin), and a phytosterol as its principal constituents.

A concentrated alcoholic extract of the bark was dissolved in water and extracted with ether, which caused the precipitation of some impure prunetin (see below), but dissolved a mixture of (1) an acid substance, m. p. 121° , crystallising in plates, and giving a reddish-purple coloration with ferric chloride solution; (2) a phytosterol, m. p. 137° , which furnished an acetyl derivative, $C_{27}H_{43}OAc$, m. p. 121° , crystallising in lustrous plates; (3) fatty matter furnishing the same phytosterol and formic, butyric, and palmitic acids on hydrolysis; (4) prunetin, $C_{16}H_{12}O_5$, m. p. 242° (corr.), which crystallises in colourless needles, dissolves in alkalis with a yellow colour, but is sparingly soluble in organic solvents. It furnishes a monoacetyl derivative, m. p. 190° , a diacetyl derivative, m. p. $221-226^{\circ}$ (corr.), and a dibenzoyl derivative, m. p. 215° , all of which crystallise well. On treatment with methyl iodide and sodium methoxide it yields a monomethyl ether, m. p. 145° , crystallising in flat, lustrous needles, and this in turn gives a monoacetyl derivative, m. p. 202° , crystallising in colourless prisms. When heated with hydriodic acid, prunetin furnishes 1 mol. of methyl iodide, and prunetol,



m. p. 290° , which crystallises in colourless needles, yields a triacetyl derivative, m. p. 205° , and on methylation furnishes a mixture of prunetin methyl ether (see above), and a second product, which is insoluble in ether and furnishes a crystalline acetyl derivative, m. p. 186° . Both prunetin and prunetol, on solution in boiling acetic acid and addition of sulphuric acid, furnish unstable sulphates of the type described by Perkin and Pate (*Trans.*, 1895, 67, 644). On fusion with potassium hydroxide, prunetin yields *p*-hydroxyphenylacetic acid and a substance which gives the reactions of phloroglucinol, and furnishes methyl iodide on treatment with hydriodic acid. It is considered that

prunetin is closely related to scutellarein (Molisch and Goldschmiedt, Abstr., 1902, i, 48) in constitution, and may have the formula



The aqueous solution, after extraction with ether, deposited on standing crystals of quercimeritrin (Perkin, Trans., 1909, 95, 2181).

The aqueous extract on defaecation with lead acetate and subsequent extraction with ethyl acetate furnished a new glucoside, *prunitrin*, $\text{C}_{20}\text{H}_{24}\text{O}_{11}$, crystallising from hot water in slender needles. This, on hydrolysis with hydrochloric acid, yielded prunetin and dextrose, and is probably the source of prunetin in the bark. Yellow colouring matters also occur in *Prunus cerasus* and *P. avium* barks.

T. A. H.

The Resistibility of Wheat and Barley to Poisons and its Importance for Sterilisation. HEINRICH SCHROEDER (*Centr. Bakt. Par.*, 1910, ii, 28, 492—505).—The following method was found to be suitable for sterilising wheat and barley grains. The seeds are first well washed in running water, and then immersed in 5% silver nitrate solution for eighteen to twenty-four hours. They are then washed with water, and allowed to swell in a dilute solution of sodium chloride.

The method would presumably be suitable for other seeds, such as rice and oats, which are protected similarly to wheat, but it does not seem suitable for sterilising leguminous seeds.

Only undamaged seeds can be sterilised with silver nitrate.

N. H. J. M.

Influence of Some Artificial Oxydases and of Some Metallic Compounds on the Growth of Wheat. V. NASARI (*Atti R. Acad. Lincei*, 1910, [v], 19, ii, 361—367).—From experiments on the germination of wheat in the laboratory and also its growth under agricultural conditions, the authors find that compounds of manganese (dioxide, sulphate, carbonate) exert a favourable influence on the result obtained. The manganese compounds were supplied to the plant in three ways: (1) as a component of an artificial oxydase, with which the seeds were enveloped; (2) as a component of a paste containing starch and nitrogenous organic matter, with which the seeds were covered; (3) as a fertiliser. Ferric oxide may also have a beneficial effect, but ferrous sulphate only prevents mildew. Copper and aluminium sulphates affected growth unfavourably.

R. V. S.

Putrefaction Bases from the Decomposition of Soy Beans (*Glycine hispida*). KIYOHISA YOSHIMURA (*Biochem. Zeitsch.*, 1910, 28, 16—22. Compare Abstr., 1909, ii, 928).—The following bases can be isolated from the products formed when soy beans are boiled with water, the moist beans rubbed in a mortar until the whole has a pasty consistency, and left for some four months at the ordinary temperature: β -amino-4-ethylglyoxaline (β -iminoazolyethylamine: Ackermann, this vol., i, 419), 0.18; tetramethylenediamine, 0.25;

pentamethylenediamine, 0.53; trimethylamine, 0.23; ammonia, 4.69. The numbers refer to grams per kilo. of air-dried material.

Histidine, arginine, and lysine could not be detected. J. J. S.

Harmlessness of Sulphurous Acid in Wines. P. CARLES (*Ann. Chim. anal.*, 1910, 15, 419—421; *Bull. Soc. chim.*, 1910, [iv], 7, 998—1001).—The author emphasises the non-injurious effects of sulphurous acid, points out the necessity of using this acid in the manufacture of certain classes of wines, and draws attention to a report recently issued (this vol., ii, 734) which deals with this subject. W. P. S.

Importance of Osmotic Pressure and of Electrolytic Conductivity in Judging Soils. JOSEF KÖNIG, JULIUS HASENBAUMER, and H. MEYERING (*Landw. Versuchs-Stat.*, 1910, 74, 1—56).—The estimation of the osmotic power of taking up water yields good results when a constant temperature (18—20°) is maintained. The process can also be employed for the estimation of the mol.-wt. of substances not, or only slightly, subject to diosmosis.

Estimation of electrolytic conductivity of soils generally yields values closely related to the osmotic power of taking up water. Both are considerably increased by the usual manures, and diminished by the growth of plants, so that both give expression to the degree of solubility of plant nutrients in the soil. Electrolytic conductivity is more readily estimated than the osmotic taking up of water; the latter seems, however, to furnish the more trustworthy results.

As electrolytic conductivity increases as the size of soil particles diminishes, a constant degree of fineness, not exceeding 1 mm., should be employed.

The potassium and phosphoric acid of dipotassium phosphate are completely absorbed up to a certain point; sulphates are partly absorbed, whilst nitrates and chlorides are not absorbed at all.

Increased yields are obtained by treating exhausted soils containing complex humates or humus colloids with hydrogen peroxide.

Growth of clover resulted in increased amounts of soluble nutrients in the soil. N. H. J. M.

The Ammonia in Soils. EDWARD J. RUSSELL (*J. Agric. Sci.*, 1910, 3, 233—245).—Soil contains a number of nitrogenous compounds that readily evolve ammonia on treatment with alkalis. In order to discriminate between these and the true ammonium compounds present, the author investigated the relationship between the concentration of alkali and evolution of ammonia when soil was distilled with alkalis under diminished pressure. The resulting curves show that two stages exist; in the first, the ammonium compounds are decomposed; in the second, other nitrogen compounds break down. The two stages are very marked when either magnesium oxide or alcoholic potash is used as the alkali, and therefore the author uses either of these in determining the ammonia free or combined in soils.

A number of determinations show that ammonia is present only in minute amounts in normal soils, although when nitrification was

stopped, marked accumulations occurred. It follows that the rate of nitrification must be greater than that of ammonia production, and in normal conditions is limited by this rate. In the light of this observation, it is shown that the various methods in vogue for studying the rate of nitrification in soil really deal with three separate things: the rate of ammonia production in soils, the rate of nitrate production in soils, and the rate of nitrification in a culture solution; the discordance of the results is therefore explained.

When ammonium salts are added to soil a certain proportion enters into a stable combination that is not decomposed on distillation with alcoholic potash or magnesia, and is therefore not an ammonium compound. Its constitution, however, has not been determined.

E. J. R.

Biochemical Resolution of Phosphoric Acid in Soils. RENATO PEROTTI (*Biol. Zentr.*, 1910, 39, 717—718; from *Staz. sper. agrar. ital.*, 1909, 42, 537—538).—The solution of phosphoric acid in ordinary soils depends on the action of acids producing bacteria, and is increased by the presence of carbohydrates, especially disaccharides, and of ammonium sulphate. Ammonium tartrate is indifferent, whilst ammonium nitrate gives sometimes positive and sometimes negative results. Calcium and magnesium carbonates retard the action of the bacteria, whilst alumina is more indifferent, and ferric oxide is somewhat favourable.

N. H. J. M.

Suitability of the Calcium of Calcium Silicate for the Nutrition of Plants. HANS MIETH (*Landw. Versuchs-Stat.*, 1910, 74, 81—120).—Calcium in the form of silicates is readily utilised by plants, and far more silica is taken up than calcium. The silicates are decomposed by plants with production of free silicic acid and calcium carbonate.

In estimating the available calcium in soils, it is necessary to include silicates as well as carbonate.

N. H. J. M.

Analytical Chemistry.

New Normal Solution and Reagent Bottle. FRANK M. DAVIS (*J. Amer. Chem. Soc.*, 1910, 32, 1277—1279).—The normal solution bottle described consists of a long, narrow bottle provided with a ground glass cap, furnished with a groove to admit air when desired. The bottle has two side-tubes, one near the top, and the other near the bottom. To these is fused a wider tube, graduated like a burette, and having a delivery tube at the lower end. This delivery tube is provided with a glass stopcock, and another stopcock is placed in the lower of the two tubes connecting the burette with the bottle.

The apparatus is supported in a light wooden frame suspended by trunnions between two triangular racks.

On opening the stopcock between the burette and bottle, adjusting the cap of the bottle so that air can enter, and tilting the apparatus forward if needful, the solution flows from the bottle into the burette. The stopcock is then closed, and the bottle replaced in an upright position. The liquid can now be drawn off from the burette as required.

The reagent bottle is of similar construction, but the burette is set into the wall of the bottle, so that the apparatus can be held in the hand, and a support is not necessary.

The advantages of these forms of apparatus are that measured quantities of the reagent can be withdrawn from the bottle without recourse to measuring cylinders or pipettes, and that the risk of extraneous matter being admitted into the reagent is obviated.

E. G.

A Very Sensitive Indicator. JULIUS F. SACHS (*Chem. Zeit.*, 1910, 34, 1192).—Radish skins are extracted for a few hours with their own weight of 96% alcohol, and should the liquid show any acidity to litmus paper, it is carefully neutralised with $N/100$ potassium hydroxide. This solution, 2 c.c. of which are added to 50 c.c. of the liquid to be tested, makes an excellent indicator for both acid and alkalis, turning intensely red with the former, and green with the latter. It is more delicate than methyl-orange or phenolphthalein, but, like the latter, it is affected by carbon dioxide.

L. DE K.

Rupp and Loose's Indicator. IWAN I. VON OSTROMISLZENSKY and I. S. BABADSCIAN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 609–611. Compare Abstr., 1908, ii, 90).—Rupp and Loose's methyl-red is a very delicate indicator for alkali hydroxides, but the authors were unable to isolate it by the method described by Rupp and Loose. By employing the theoretical quantity of dimethylaniline, extracting the products of reaction with ether or chloroform, and evaporating the latter, the substance was isolated, but it could not be purified by recrystallisation.

Z. K.

A Delicate Reaction for Hydrogen. CONSTANTIN ZENGELS (*Zeitsch. anal. Chem.*, 1910, 49, 729–732).—The process is based on the fact that platinum and palladium absorb hydrogen, and then exercise a reducing action when heated with molybdenum solution. This is made by dissolving 1 gram of molybdenum trioxide in dilute sodium hydroxide, acidifying the liquid with hydrochloric acid, and diluting to 200 c.c.

The gas to be tested is first passed through a wash-bottle containing aqueous sodium hydroxide. The end of the delivery tube dipping into a test-tube containing a few c.c. of the reagent is tied over with platinum gauze, and if hydrogen is present in not too minute a quantity, the solution will turn blue.

A still more delicate test is to allow the gas to come in contact with spongy palladium heated at 80–120° in an atmosphere of carbon dioxide. A convenient apparatus is described for this purpose. The

palladium is then warmed with molybdenum solution to see if there is any reduction.

L. DE K.

Electrolytic Estimation of Chlorine in Hydrochloric Acid with the Use of a Silver Anode and a Mercury Cathode. JACOB S. GOLDBAUM and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, 32, 1468—1471).—As a result of criticism of the electrolytic method (*Abstr.*, 1907, ii, 574, 988; 1908, ii, 1072) for the estimation of chlorine when applied to solutions containing free hydrochloric acid, the authors have made further experiments. It is shown that satisfactory results can be obtained if certain precautions are taken. Silver is deposited on the platinum gauze anode by electrolysis of a cyanide solution, and the electrode is then dipped in dilute hydrochloric acid, washed thoroughly with distilled water, and ignited to incipient redness in a Bunsen flame. By this means any admixed cyanide is completely removed.

To obviate the disturbing effect of the formation of oxide on the anode, the latter is placed for ten to fifteen minutes in an electric oven heated to 300°, when the silver oxide is completely decomposed.

Experimental data are recorded which show that the estimation of chlorine in hydrochloric acid can be effected without appreciable error if the above precautions are observed. Similar data are given for the electrolytic estimation of bromine and hydrobromic acid, but the results appear to be rather low.

H. M. D.

Catalytic Action of Silver Salts [on Chlorates in Presence of Aniline Hydrochloride]. JUAN PAGES VIRGILI (*Anal. Fis. Quim.*, 1910, 8, 222—226).—Traces of silver very much intensify the colour produced by the action of a chlorate on the solution of aniline hydrochloride employed in the author's method of estimating chlorates colorimetrically (*Abstr.*, 1909, ii, 179). It is therefore necessary if silver nitrate has been used as a means of removing other substances present (for example, ferri-cyanides) to ensure that any excess of silver is eliminated by the addition of sodium chloride before proceeding to estimate chlorates. The manner in which the silver acts is uncertain, but possibly it exerts a catalytic action, by which the velocity of the change producing the coloration is accelerated. The sensitiveness of the method formerly described can be much increased by adding one or two drops of a 1% solution of silver nitrate before adding the aniline reagent; in presence of silver, traces of chlorate, which ordinarily cannot be detected or estimated, give a distinct coloration. Thus 2 grams of sodium nitrate containing 0.00005 gram of chlorate usually gives a coloration only after several minutes; in presence of silver, 0.2 gram of the nitrate produces far more coloration after a few seconds. This simplifies the examination of refined nitrates containing less than 0.0001 gram of chlorate.

Traces of copper and of chloroplatinic acid exercise a similar action to silver in increasing the colour, but, unlike silver, they appear to retard its production.

W. A. D.

Weselszky's Method for Estimating Bromine and Iodine. JOSÉ CASARES GIL (*Anal. Fis. Quim.*, 1910, 8, 33—40).—Tests made

of the accuracy of Weszelszky's method (Abstr., 1900, ii, 436, f.), estimating the amount of iodine in known weights of dissolved iodide showed that heavy loss of iodine occurs if attempts are made to remove by direct evaporation the excess of chlorine used in oxidising the iodide to iodate. If, however, the excess of chlorine is eliminated by aspirating a rapid current of air through the hot acid solution, accurate results are obtained.

Contrary to Weszelszky's statement, potassium chlorate liberates traces of iodine from potassium iodine in presence of hydrochloric acid under the conditions used in the method; on adding 0.029 gram of potassium chlorate dissolved in 125 c.c. of distilled water to 5 c.c. of 10% potassium iodide and 5 c.c. of hydrochloric acid, 3 drops of $N/10$ sodium thiosulphate are required to destroy the iodine, using starch as indicator in the usual way. If the chlorate is dissolved in only 15 c.c. of water, 5 drops of $N/10$ thiosulphate are required. To convert the sodium hypochlorite formed during the oxidation of bromides in Weszelszky's method by chlorine in alkaline solution entirely into chlorate, it is absolutely necessary to evaporate to dryness and heat the residue for some time on the water-bath. Control analyses made with pure potassium bromide show that Weszelszky's method gives fairly accurate results.

W. A. D.

Precipitation of Sulphate Ions as Barium Sulphate. EXSR RUPPIN (*Chem. Zeit.*, 1910, 34, 1201).—The following method is recommended. The solution (250 c.c., furnishing about 1.5 grams of barium sulphate) is slightly acidified with hydrochloric acid and heated to boiling. Boiling solution of barium chloride (200 grams per litre) is then added all at once in excess of about 50%, and the whole set aside until the following day. The mother liquor is decanted through a filter, and the precipitate digested with 125 c.c. of very dilute nitric acid during fifteen minutes, the clear liquid being decanted through the same filter, and the filtrate and washings collected and concentrated to 200 c.c. To this, 2 c.c. of saturated barium nitrate solution are added, and after thirty minutes the precipitate is filtered off and washed. The main precipitate is then collected on a filter and dried at 100°. The two filter papers are burnt and their ash added to the precipitate, and the whole ignited and weighed with the usual precautions.

A less accurate, but quicker, method consists in precipitating the sulphate by the use of a 20% solution of barium chloride in an excess of about 33%, filtering after about thirty minutes, washing the precipitate with about 100 c.c. of boiling water by decantation, and continuing the washing on the filter paper until the wash-water is free from chlorides.

T. A. H.

Estimation of Organic Matters in Spent Sulphuric Acids. RUD. MICHEL (*Chem. Zeit.*, 1910, 34, 1210—1211).—The apparatus consists of a round-bottomed flask fitted with a stopcock funnel, and connected by means of a bent capillary tube to the three-way tap of an ordinary gas burette filled with water. Into the flask are introduced 20 c.c. of a saturated solution of potassium permanganate, and into

the funnel is placed a known volume of the acid to be tested. The tap at the lower end of the burette being opened, the acid is admitted slowly into the flask, when carbon dioxide is evolved and enters the burette. The remaining gas is expelled from the flask by introducing water through the funnel until the liquid reaches the three-way tap. The burette is now closed, and the volume of gas read off with the usual precautions. The exact volume of carbon dioxide is then found by absorption with aqueous potassium hydroxide in the usual manner.

The carbon dioxide is calculated to its weight of carbon; 75 parts of the latter average 100 parts of (resinous) organic matter.

L. DE K.

Use of Nitron in the Analysis of Nitrates. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 567—570. Compare Gutbier, Abstr., 1905, ii, 418).—A somewhat modified form of Busch's gravimetric estimation of nitric acid in nitrates by means of nitron.

The weighed substance is dissolved in 100 c.c. of water and boiled, after which 10—12 drops of dilute sulphuric acid are added for every 0.1 gram of NO_3 , and 10 c.c. of a 10% solution of nitron in 5% acetic acid. After cooling, the beaker is surrounded by ice for five to eight hours, at the end of which time the solution is filtered through a Gooch crucible containing Swedish filter paper instead of asbestos. The precipitate is washed five to seven times with 3—5 c.c. of a saturated solution of nitron nitrate cooled to 0° , and finally once with 3—5 c.c. of water at 0° . It was then dried at 105° — 110° . The method gives good results, and is evidently independent of the nature of the metal.

Z. K.

Detection and Estimation of Arsenic Acid in Presence of Arsenious Acid by means of Magnesia Mixture. JOHANNES C. BRUNNICH and F. SMITH (*Zeitsch. anorg. Chem.*, 1910, 68, 292—296).—The experiments of Lutz and Swinne (Abstr., 1909, ii, 1052) have been repeated, using weaker arsenite solutions, such as are employed for agricultural analyses. The best results are obtained by using a magnesia mixture containing 5.5% magnesium chloride, 10.5% ammonium chloride, and only 1.4% ammonia. With such a solution a distinct crystalline precipitate is obtained in ten minutes from a solution containing only 0.0002 gram As_2O_3 , alone or in the presence of 0.025 gram As_2O_3 . The addition of ammonia, although generally recommended, is disadvantageous.

The separation is quantitative if the quantity of arsenite present does not much exceed 0.5% As_2O_3 . The quantity of alkali salts present should not exceed an original content corresponding with 1% NaOH . Citrates completely prevent the precipitation of arsenates.

C. H. D.

Apparatus for the Estimation of Carbon, Arsenic, and Sulphur in Iron and Steel. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1910, 23, 1980—1981).—The apparatus is essentially the same as that described and figured previously (this vol., ii, 893). It consists of

employed. Further work on this subject has now been carried out. The alkaline-earth metals were used, and the acetate, formate, and lactate electrolytes described by Davison (*Abstr.*, 1905, ii, 854). Corresponding separations were made with low currents (0.3 ampere) and with high currents (5 amperes).

The results show that low currents are preferable for the deposition of cadmium when organic electrolytes are used. It was observed that each electrolyte exerts a marked influence on the character of the deposit. The best deposits were obtained in presence of a mixture of ions, and especially in presence of the sulphate ion. * The formate ion exercises a good influence on the character of the deposit, cadmium acetate solution with the formate electrolyte, and cadmium formate solution with the lactate electrolyte, giving satisfactory results, even in presence of the alkaline-earth metals. The acetate and lactate electrolytes when used alone were not so successful.

E. G.

Colorimetric Estimation of Lead in Potable Water. K. SCHERINGA (*Pharm. Weekblad*, 1910, 47, 1212—1213. Compare Egeling, *Abstr.*, 1907, ii, 398).—From the results of experiments, the author concludes that Egeling's colorimetric method for the estimation of lead in potable water is untrustworthy.

A. J. W.

Electrolytic Separations. IRVING H. BUCKMINSTER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, 32, 1471—1477).—The results of a large number of experiments relating to the separation of pairs of metals by electrolysis are communicated. The conditions under which the following separations were effected are briefly described: Mercury and bismuth from nickel in presence of sulphuric acid; copper, mercury, and lead from nickel in presence of nitric acid; zinc from nickel in an alkaline tartrate solution; copper from nickel in presence of free phosphoric acid. Silver also can be separated from nickel in presence of free nitric acid if a little alcohol is added to the solution. In the separation of nickel from aluminium in an ammoniacal ammonium sulphate solution, the deposited nickel is contaminated with aluminium hydroxide; if, however, a little sodium hydroxide is added, the hydroxide is dissolved, and good results are obtained. Nickel can also be separated from magnesium, and the alkaline-earth metals in an ammoniacal ammonium salt solution. From this solution nickel is not deposited if chromium or cobalt salts are present, and it has been found that cobalt-ammonia compounds are formed in the latter case.

Other experiments have reference to the deposition of zinc from a cyanide solution, the separation of silver and mercury from bismuth in nitric acid solution, of uranium from zinc, and of cobalt and nickel from uranium.

H. M. D.

Conditions Affecting the Electrolytic Estimation of Copper. WALTER C. BLASDALE and W. CRUES (*J. Amer. Chem. Soc.*, 1910, 32, 1264—1277).—The difficulties encountered in the application of the

electrolytic method to the analysis of pyritiferous ores are enumerated, and means are indicated for overcoming them.

When 1 gram samples of such ores are used, the resulting solution may possibly contain 0.2 gram of copper, 0.4 gram of iron, and variable quantities of zinc, arsenic, and lead. If arsenic is absent, the copper can be completely separated within ninety minutes by the use of the Winkler electrode and a current of 0.75 ampere, provided that the volume does not exceed 100 c.c. and the solution does not contain any nitric acid or more than 5 c.c. of concentrated sulphuric acid. If arsenic is present, the solution should be electrolysed under the conditions already specified, and the deposit dissolved in nitric acid and again electrolysed; or, if the amount of arsenic is small, good results can be obtained by a single precipitation if 1–2 c.c. of nitric acid and 5 grams of carbamide are added to the solution. E. G.

Collection of Colloidal Precipitates. MORTON LIEBSCHUTZ (*Chem. News*, 1910, 102, 213).—In the analysis of bronzes, the tendency of metastannic acid to pass through the filter may be overcome by heating it with a dilute solution of albumin, which coagulates the colloidal precipitate. The latter has afterwards to be boiled with dilute nitric acid to remove adsorbed copper.

In separating zinc and copper by the cyanide method, the copper cyanide is removed by decantation, and to the solution containing the zinc sulphide in suspension, a little lead acetate is added. The zinc and lead sulphides can then readily be collected; the former is dissolved by boiling with dilute hydrochloric acid, and titrated with potassium ferrocyanide. G. S.

Estimation of "Carborundum" in Fragments of Coke Crucibles. HENRYK WDOWISZEWSKI (*Chem. Zeit.*, 1910, 34, 1200–1210).—One gram of the finely-powdered material is ignited to burn the coke, and the weighed residue is analysed as usual for silica and bases. If carborundum is present, it is obvious that the sum total of the various constituents must exceed 100%; by multiplying the excess by two, the amount of carborundum is obtained.

The accuracy of the result, of course, depends on the care bestowed on the analytical operations. L. DE K.

Assay of Aluminium Ores. JUAN CALAFAT Y LEÓN (*Anal. Fis. Quim.*, 1910, 8, 281–286).—To ascertain whether a mineral is suitable as a source of aluminium, roughly 0.5 gram of the finely powdered substance is intimately mixed with an equal volume of powdered anhydrous sodium carbonate and heated on charcoal in an oxidising flame during several minutes. The product is extracted with water, the solution filtered, and carbon dioxide passed through the filtrate. If the ore is of any value as a source of aluminium, the carbon dioxide will precipitate aluminium hydroxide from the solution of aluminate. The method can be made roughly quantitative by comparing the height of the precipitate obtained after settling in a tube of fixed diameter with that obtained from 0.5 gram of bauxite under similar conditions. The method is very rapid, and is useful when a large number of

minerals have to be examined to ascertain their fitness as ores of aluminium. Ordinary clay, kaolin, and other forms of aluminium silicate do not indicate the presence of alumina in this test.

W. A. D.

Detection and Estimation of Manganese in Wine. DUMITRESCU and (Mlle.) E. NICOLAU (*Ann. Falsif.*, 1910, 3, 407—410).—When the ash of a wine containing manganese is heated with ammonium persulphate solution in the presence of a trace of cobalt nitrate, the pink permanganate coloration obtained is not proportional to the amount of manganese present, as the latter is partly precipitated as its hydroxide. It is therefore recommended that the heating be prolonged for thirty minutes, and that the cobalt nitrate be omitted when it is desired to estimate the quantity of manganese present. Under these conditions the whole of the manganese is precipitated, and may be collected and weighed. The authors have estimated the quantity of manganese in 52 samples of various white and red wines, the quantities found varying from 1.8 to 27 mg. per litre.

W. P. S.

Electrolytic Separation of Nickel and Cobalt. PIERRE BRUYLANTS (*Bull. Soc. chim. Belg.*, 1910, 24, 367—372).—The description given by Piñera Alvarez of his method for the electrolytic separation of nickel and cobalt is not detailed enough, and the author has not been able to obtain satisfactory results. Both the metal deposited and the solution remaining after electrolysis contained nickel and cobalt, and the results are not even approximately accurate.

The following method is suggested: To a solution containing the sulphates of nickel and cobalt is added potassium cyanide until the precipitate first formed just redissolves. The solution is then oxidised with bromine water and acid added. The nickel ions thus produced form nickel cobalticyanide, which is insoluble in acids, but soluble in ammonium hydroxide, giving a solution containing the ions $\text{Ni}(\text{NH}_4)_4^{++}$ and $\text{Co}(\text{CN})_6^{--}$. Electrolysis of the resulting solution, using Sand's apparatus and a graded potential, leads to the deposition of nickel, but in all the experiments so far carried out the nickel has contained 2—4% of cobalt.

T. S. P.

Estimation of the Amount of Molybdenum in Calcium Molybdate. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1910, 23, 1981).—0.5 Gram of the finely-powdered compound is boiled with 20 c.c. of strong hydrochloric acid and 1—2 c.c. of strong nitric acid. The solution is diluted to 150 c.c., and, without filtering, poured into an excess of ammonia, to which a few c.c. of yellow ammonium sulphide have been added. After heating for a few minutes on the water-bath, the solution is filtered, and the undissolved matter is washed with dilute ammonia containing a little ammonium sulphide. From the filtrate the molybdenum trisulphide is recovered by adding dilute hydrochloric acid, and it is then converted in the usual way either into molybdenum disulphide or trioxide.

L. DE K.

Estimation of Tin in White Metals by Electrolysis.
E. SCHÜRMANN (*Chem. Zeit.*, 1910, 34, 1117—1118).—One gram of the alloy is covered with 10—15 c.c. of 50% solution of tartaric acid, and nitric acid, D 1.4, is then gradually added until the metal is dissolved. The solution is then diluted to 300 c.c., heated to boiling, and the tin precipitated by adding 10 c.c. of a 25% solution of sodium hydrogen phosphate in weak nitric acid. After diluting to about 600 c.c. with boiling water, the tin phosphate is allowed to settle, the liquid is siphoned off, and the precipitate washed by decantation with 300 c.c. of a 1% solution of potassium nitrate acidified with nitric acid. The washings are heated on the water-bath, when a further deposit is obtained, which is collected on a filter, and the main precipitate is then added. When drained, the precipitate is transferred to the beaker, in which the precipitation took place, and the little remaining in the filter is dissolved by means of 25 c.c. of hot *N*-potassium hydroxide. The alkaline liquid is then poured into the beaker, and, on warming, the tin phosphate soon dissolves. The solution is now neutralised with oxalic acid solution, and another 5 grams of the solid acid are added. Into the solution, occupying about 300 c.c., is passed, at boiling heat, a rapid current of hydrogen sulphide to remove any traces of antimony and copper. The filtrate is concentrated to 150 c.c., and neutralised with 80% aqueous potassium hydroxide; another 5 c.c. of the same are then added. The solution is then submitted to electrolysis, by preference in a Frary apparatus, using a current of 6—8 amperes and 4—5 volts; the operation is ended in two to two and a-half hours.

The process is also applicable to electrolytic tin. It does not give a clear solution with the tartaric-nitric acid mixture, but this makes no difference, as the separated stannic acid is dissolved afterwards by the potassium hydroxide. L. DE K.

Estimation of Gold by means of Hydrogen Peroxide.
L. RÜSSLER (*Zeitsch. anal. Chem.*, 1910, 49, 739—740).—Gold may be estimated by reduction with hydrogen peroxide in presence of sodium hydroxide. The author states that the addition of alkali is not strictly necessary, as the reduction also takes place in acid solution, but, owing to the fact that the operation takes a great many hours, the process is not of any practical value.

In presence of lithium or, preferably, potassium carbonate, the reduction is soon completed, and this fact may be utilised for gravimetric estimations of gold. L. DE K.

Detection of Ethyl Alcohol in Presence of Methyl Alcohol.
GEORGES DENIGES (*Bull. Soc. chim.*, 1910, [iv], 7, 951—952. Compare this vol., ii, 357, 461).—The process depends on the fact that whilst bromine water has but little oxidising action on warm methyl alcohol, it converts ethyl alcohol on warming into acetaldehyde. The latter is detected by its power of restoring the colour to a solution of magenta decolorised by sodium hydrogen sulphite and hydrochloric acid. It is always advantageous to have a little methyl alcohol present, since this reacts with acetaldehyde to form dimethylacetal,

thus avoiding possible loss of the aldehyde. Details of the method of applying the test are given. T. A. H.

Estimation of Ethyl Ether and Benzene in Alcohol. HANS WOLFF (*Chem. Zeit.*, 1910, 34, 1193).—The process is similar to the one recommended by Holde and Winterfeld (*Abstr.*, 1908, ii, 435). One hundred c.c. of the spirit to be tested are diluted to D 0.96, and then submitted to distillation, the distillate being collected in a graduated cylinder. When 20 c.c. have passed over, 80 c.c. of brine are added, and the whole is thoroughly shaken. The volume of ether or benzene is then read off. The results are satisfactory, although a trifle too low, particularly in the case of ether. L. DE K.

Estimation of Phenol in the Urine of Oxen. CARL NEUBERG and A. HILDESHEIMER (*Biochem. Zeitsch.*, 1910, 28, 523—528).—Mooser's statement (this vol., ii, 1039) that phosphoric acid may be used for the direct iodometric estimation of phenol and cresol in herbivorous urine is incorrect. The older modifications of the Kessler-Penny process must be employed both for diabetic urines and the urine of herbivora (on account of the glycuronic acid, pentoses, etc., in it). W. D. H.

Analysis of Cellulose Nitrates, Glycerol Nitrates, and Other Compounds from which Nitric Acid is Liberated by Concentrated Sulphuric Acid. EMILE BRONNERT (*Bull. Soc. ind. Mulhouse*, 1910, 80, 251—259).—Stannous sulphate or stannous potassium sulphate is dissolved in 50 vol. % sulphuric acid, and a little hydrochloric acid is added to obtain a clear solution. This is then standardised as follows: 0.15 gram of pure potassium nitrate is dissolved in a few drops of water, and 50 c.c. of sulphuric acid and one drop of solution of diphenylamine are added. The tin solution is then run in from a burette until the bluish-violet colour has completely disappeared. The tin solution is then diluted with 50 vol. % sulphuric acid until it is of $N/10$ -strength.

By means of this solution, commercial nitrates, spent acids, and also nitro-compounds, such as cellulose nitrates, which liberate nitric acid when dissolved in sulphuric acid, may be readily assayed. Attention is called to the uneven composition of some samples of commercial nitro-cellulose. L. DE K.

Estimation of Sugar by Reduction of Colouring Matters. NEUMANN WENDER (*Biochem. Zeitsch.*, 1910, 28, 523—524).—A question of priority. The method described by Hasselbalch and Lindhard (this vol., ii, 905) as new, has been in use for many years (Crismer, 1888; Wender, 1890). W. D. H.

A Simple Method for the Estimation of Sugar in the Blood. II. The Sugar in the Blood. K. MÖCKEL and E. FRANK (*Zeitsch. physiol. Chem.*, 1910, 69, 85—88. Compare this vol., ii, 554).—By care in one or two points of detail, the method previously described can be utilised for the correct estimation of sugar in the blood, as well as in serum. W. D. H.

The Reducing Substances of Urine. CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1910, 69, 72—75. Compare Abstr., 1909, ii, 902).—When known weights of dextrose are added to urine and the mixture titrated by Bertrand's method (Abstr., 1907, ii, 136), the amounts of dextrose found agree extremely well with the amounts added. When blood charcoal is used as a clarifying material before the estimation, the results are apt to come low. The addition of concentrated solutions of uric acid, creatinine, or urochrome to solutions of dextrose does not interfere with the estimation of the sugar; the reduction is the sum of the reductions of the dextrose and of the nitrogen compound. A loss is found, however, in working with dilute solutions, and this loss increases with the dilution. This is attributed to the diminution of the reduction of uric acid, urochrome, and especially of creatinine with an increase in dilution. This accounts for the fact that these substances possess no reducing properties in urine. The author suggests that the amount of creatinine present in normal urine is less than that usually accepted (0.6–2.1 grams per day), as normal urine shows no reducing action, whereas a solution containing this amount of creatinine is strongly reducing. J. J. S.

Reactions of Carbohydrates. I. Sucrose. C. REICHARD (*Pharm. Zentr.-h.*, 1910, 51, 979–986).—A detailed description is given of the colour and other changes which take place when various reagents are allowed to react with solid sucrose.

Sulphuric, nitric, or hydrochloric acid, in the cold, converts sugar into a sticky mass, which does not dry on exposure to air. Sulphuric acid does not cause the separation of carbonaceous matter unless the preparation is heated. The green mixture of cupric sulphate and hydrochloric acid remains bright green much longer when sucrose is present. Sucrose inhibits to some extent the precipitation of mercurous chloride when hydrochloric acid is added to mercurous nitrate. A mixture of sodium arsenate with hydrochloric acid and sucrose gives a stable rose-red coloration. In presence of hydrochloric acid, sucrose gives a dark green coloration with potassium dichromate, blue with ammonium molybdate, and brown, changing to violet, with ammonium vanadate, but no coloration with sodium tungstate or with titanous acid in presence of sulphuric acid. A number of colour reactions with organic substances are also described, the most interesting of these are the red coloration given with tannic acid in presence of hydrochloric acid, and the gooseberry-red tint obtained with resorcinol and hydrochloric acid. The last two reactions and that with arsenic acid may be suitable for the detection of sucrose.

T. A. H.

Detection of Dextrin by means of its Coloration by Iodine. GEORGES RIVAT (*Chem. Zeit.*, 1910, 34, 1141).—Whilst a 1% iodine solution in water gives blue colorations of equal intensity with pure starch or with a mixture of starch and dextrin, a solution of 0.00012 gram of iodine in 1 c.c. of water gives a blue coloration at once with pure starch, but not with a mixture of starch and dextrin. In

the latter case the quantity of iodine that must be added before a blue tint is developed seems to vary with the amount of dextrin present. The observation may prove on further investigation to be the basis of a method of examining mixtures of starch with dextrins.

T. A. H.

Modification of the Phenylhydrazine Reaction. JACOB BÖESEKEN (*Chem. Weekblad*, 1910, 7, 934).—As a substitute for phenylhydrazine, the author employs a solution of the base in sulphurous acid, which will dissolve up to 10%. This solution contains compounds of the formulae $C_6H_5N_2H_3SO_2$ and $(C_6H_5N_2H_3)_2SO_2$, and is prepared by passing washed sulphur dioxide through a mixture of phenylhydrazine and the requisite quantity of water until solution is complete. At first a crystalline compound separates, but on further passage of the gas, it re-dissolves. Impurities are then filtered off. The reagent reacts at once with soluble aldehydes and ketones, and, on warming, with insoluble carbonyl compounds, the hydrazones being obtained in the pure state. Its efficacy has been tested with formaldehyde, acetaldehyde, acetone, benzaldehyde, *m*-nitrobenzaldehyde, acetophenone, cuminaldehyde, furfuraldehyde, *p*-chloroacetophenone, levulinic acid, acetylacetone, acetonylacetone, and ethyl acetoacetate.

When warmed with monoses at 80°, the reagent yields pure osazones. It has been tested with dextrose, levulose, *d*-galactose, *d*-mannose, *l*-xylose, and rhamnose.

A. J. W.

New Method for Estimating Volatile Fatty Acids. ERNST WELDE (*Biochem. Zeitsch.*, 1910, 28, 501—522).—This is a method of steam distillation in a vacuum. The distillation lasts two hours; the temperature is 60°; proteins, fats, and carbohydrates remain unaltered, and bacterial action is inhibited. If acid is not added, the distillate contains the free volatile acids; if phosphoric acid is added, the total volatile acids are obtained. Illustrative experiments with milk, and contents of stomach and intestine are appended.

W. D. H.

Estimation of Formic Acid [in Formates]. ALFRED F. JOSEPH (*J. Soc. Chem. Ind.*, 1910, 29, 1189—1190).—The process is based on the oxidation of formic acid by bromine water and the formation of free hydrobromic acid.

A few grams of the formate are dissolved to 200 c.c. of water, and, if necessary, made exactly neutral. Ten c.c. of the liquid are heated to boiling, and bromine water is added until the colour no longer disappears. The excess of bromine is then expelled by boiling, and the liquid titrated as usual with standard alkali. In the case of sodium formate, 1 mol. of hydrogen bromide = 1 mol. of formic acid. A correction should be made for any acidity present in the bromine water employed.

In the presence of acetic acid, the titration process cannot be employed, but the formic acid may be calculated from the amount of total bromine left after boiling; this is best estimated by Volhard's thiocyanate method. In the case of sodium formate, 2 atms. of bromine = 1 mol. of formic acid.

L. DE K.

Fission of Chloroform and Carbon Dioxide from Trichloroacetic Acid. ROBERT STOLLÉ (*Ber. Deut. pharm. Ges.*, 1910, 20, 371—372).—When trichloroacetic acid is heated in the presence of water and antipyrine, carbon dioxide and chloroform are evolved, and the latter substance may be detected by its odour. As a test for trichloroacetic acid, the author considers the use of antipyrine to be preferable to potassium hydroxide, as prescribed by the German Pharmacopœia, or to aniline (*Abstr.*, 1906, i, 159); boiling with an excess of potassium hydroxide would not distinguish between trichloroacetic acid and chloral hydrate, whilst aniline has an odour which might mask that of the liberated chloroform. The author has prepared antipyrine trichloroacetate, m. p. 75°; it is a crystalline substance and is unstable. W. P. S.

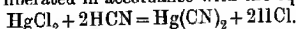
A Reaction of Nopio Acid. ODDULIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1910, 8, 328—331).—To the solution of sodium nopate in a porcelain dish, 0.1 gram of resorcinol is added, and then 10—15 grams of concentrated sulphuric acid are poured gently on to the mixture. On gently warming for a few minutes, a violet coloration appears at the zone of contact of the two liquids, which changes first to intense blue and then to green, which persists. The above colour indication is given only by resorcinol, not by the isomeric dihydroxybenzenes, or by ordinary phenol, thymol, the naphthols, etc. The trihydroxybenzenes also fail to give a coloration, with the exception of p-borogluic acid, which produces an intensely yellow coloration. The blue substance produced by sodium nopate in this test is insoluble in ether, is destroyed by water, and turns yellowish-red in presence of amyl alcohol. Some suggestions are given as to its possible nature. W. A. D.

Colorimetric Estimation of Hydrogen Cyanide. A. CHASTON CHAPMAN (*Analyst*, 1910, 35, 469—475).—The author shows that when a cyanide is treated with alkaline picrate solution, the product of the reaction may be either potassium isopurpurate or alkali salts of nitroamino-phenols; the isopurpurate is formed only when the cyanide is in excess, whilst an excess of picrate results in the formation of the nitroamino-phenols. In testing for cyanides, the picrate is usually in excess, and isopurpurate is not formed. The production of the nitroamino-phenols is the result of the reducing action of the cyanide, but other substances, such as acetone, aldehyde, hydrogen sulphide, etc., are also capable of reducing the picrate. If the reaction be employed for the colorimetric estimation of hydrogen cyanide, steps must be taken to prove that the coloration obtained is due to the presence of this substance alone. Small quantities of hydrogen cyanide may, however, be estimated by the process, provided that certain definite conditions prescribed by the author be observed, but the test has, for the reasons mentioned, a very limited sphere of usefulness.

W. P. S.

Volumetric Estimation of Hydrogen Cyanide, Especially in and with Benzaldehydecyanohydrin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, 248, 529—533).—The process is a modification

of Andrews' method (Abstr., 1903, ii, 695). The indicator, iodo eosin and ether, is not affected by hydrogen cyanide, but is changed by the hydrochloric acid liberated in accordance with the equation:



The solution under examination, containing not more than 1% of hydrogen cyanide, is treated with *N*/10-sulphuric acid or potassium hydroxide in the presence of the indicator until the aqueous liquid is just rose-coloured. A solution of mercuric chloride (27.1 grams of mercuric chloride and 11.7 grams of sodium chloride in 500 grams of water), neutral to the indicator, is added, and the mixture is at once titrated, with shaking, with *N*/10-potassium hydroxide until the rose tint is restored in the aqueous liquid.

The total hydrogen cyanide in a solution containing benzaldehyde-cyanohydrin and free hydrogen cyanide is estimated as follows. The solution is first made neutral to the indicator. Then such an excess of *N*/10-potassium hydroxide is added that after shaking vigorously for a minute adding the mercuric chloride solution, and again shaking for a minute, the aqueous liquid is coloured strongly red; *N*/10 acid is added until the colour has disappeared, and the end-point is finally obtained by titrating back with *N*/10-alkali. The changes are shown by the equations: (i) $\text{HCN} + \text{KOH} = \text{KCN} + \text{H}_2\text{O}$; (ii) $\text{KOH} + \text{CHPh}(\text{OH})\cdot\text{CN} = \text{KCN} + \text{Ph}\cdot\text{CHO} + \text{H}_2\text{O}$; (iii) $2\text{KCN} + \text{HgCl}_2 = \text{Hg}(\text{CN})_2 + 2\text{KCl}$.

The estimation of the free hydrogen cyanide in a solution containing hydrogen cyanide and benzaldehyde-cyanohydrin is performed as follows. Ten c.c. of the solution are run into a separating funnel containing about 20 c.c. of a neutralised, saturated solution of sodium sulphate (in which benzaldehyde-cyanohydrin is practically insoluble), 50 c.c. of ether and 10 drops of the 0.2% alcoholic iodo eosin are added, and the mixture is rendered neutral. After adding the mercuric chloride solution, the mixture is shaken thoroughly, and the aqueous layer is run into a vessel containing neutralised distilled water; the separating funnel is rinsed with a little sodium sulphate, and its contents are again shaken with 20 c.c. of the same solution. The aqueous liquid is run off, and, after again rinsing the funnel, the combined aqueous extracts, which contain an amount of hydrochloric acid equivalent to the free hydrogen cyanide in the original solution, are titrated with *N*/10-alkali as in the first case above. C. S.

Estimation of Citric Acid in Lemon Juice and Commercial Citrates. MATTEO SPICA (*Chem. Zeit.*, 1910, 34, 1141—1143).—The method depends on the measurement of the volume of carbon monoxide produced when citric acid is heated with sulphuric acid, and a special apparatus for the purpose is described.

An Erlenmeyer flask is closed by a hollow glass stopper forming part of the continuation of an open cylindrical dropping funnel, provided with a three-way cock, and passing through this a glass tube prolonged into the flask, whereby a stream of carbon dioxide can be introduced and passed through the flask. The terminal opening of the three-way cock is connected to a nitrometer. For each estimation, 2 grams of the citrate are placed in the flask, a little water added, and then carbon

dioxide is passed through until all air is expelled, as shown by complete absorption of the issuing gas in potassium hydroxide solution. Sulphuric acid (25 c.c.) is then run in from the dropping funnel, and carefully mixed with the citrate by shaking. The mixture is heated at from 80° to 100° and shaken continuously, the current of carbon dioxide being still maintained, and the issuing gas collected and measured with the usual precautions in the nitrometer filled with potassium hydroxide solution. One c.c. of carbon monoxide at 0°/760 mm. is equivalent to 0.009407 gram of citric acid. Carbonates may be estimated in commercial citrate by placing the weighed citrate in the flask, connecting up to a nitrometer filled with water, adding 25 c.c. of hydrochloric acid, and collecting and measuring the displaced air, which, after deducting 25 c.c. for the acid added, gives the volume of carbon dioxide formed.

T. A. H.

Characterisation of Glycuronic Acid in Urine. R. BERNIER (*J. Pharm. Chim.*, 1910, [vii], 2, 401—406).—Directions are given for the detection of glycuronic acid in urine by means of Tollens and Rorive's naphtharesorcinol reaction (*Abstr.*, 1908, ii, 638; compare Mandel and Neuberg, *ibid.*, ii, 993), and by means of phenylhydrazine (Grimbert and Bernier, this vol., ii, 163, and Grimbert and Turpaud, *ibid.*, ii, 979).

Tollens and Rorive's reaction may be vitiated by the presence of indoxyl, and to avoid this difficulty the urine should first be defaecated with mercuric acetate. All the urines tested gave positive results with this reaction, thus affording a further proof that glycuronic acid is a normal constituent.

T. A. H.

Detection of Benzoic Acid in Meats and Fats. KARL FISCHER and O. GUENERT (*Zeitsch. Nahr. Genussm.*, 1910, 20, 580—583).—The following process for separating benzoic acid from a sample of meat or fat is described as being more useful and trustworthy than that described previously by the authors (*Abstr.*, 1909, ii, 708); it is a modification of the process recommended by von der Heide and Jakob (this vol., ii, 359). Fifty grams of the material are heated with 150 c.c. of a 1% sodium hydrogen carbonate solution, the aqueous layer is then separated, neutralised with sulphuric acid, and treated with copper sulphate and sodium hydroxide. The mixture is then rendered slightly acid, filtered, the filtrate is acidified with sulphuric acid, and extracted with ether. The ethereal extract is now evaporated, and the residue obtained is tested for the presence of benzoic acid. For this purpose the test proposed by Jonescu (this vol., ii, 527) is the most trustworthy; it will detect the presence of 0.006% of benzoic acid in butter. Care must, however, be taken that only 1 mg. or so of the acid be employed in the test, and that a minimum quantity of hydrogen peroxide be used. The authors find that Robin's modification of Halphen's test is not suitable for identifying the benzoic acid extracted from fats, although it is capable of detecting very small quantities of pure benzoic acid.

W. P. S.

Absorption Spectrum of Oils. RÉNE MARCILLE (*Ann. Falsif.*, 910, 3, 423—425).—The absorption spectrum of certain oils is due to

the presence of chlorophyll or its derivatives, the bands observed corresponding with the spectrum exhibited by this substance. Olive oil shows three bands, the principal one being at λ 665, whilst cotton-seed oil and sesamé oils show feeble absorption bands. Other oils, as a rule, do not exhibit absorption spectra unless they contain chlorophyll; this is sometimes the case with commercial linseed oil and castor oil. When the oils are heated with water, the position of the absorption bands is altered slightly.

W. P. S.

Primary and Secondary Bromine Numbers of Oils. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1910, 23, 2077—2078).—When a drying oil is dissolved in a suitable solvent and the solution treated with successive small quantities of bromine, the latter is absorbed until a point is reached where a trace of free bromine remains in the solution; the quantity of bromine thus absorbed constitutes the primary bromine number of the oil. A considerable excess of bromine must then be added in order that the oil may absorb a quantity of bromine corresponding with complete saturation of the oil. The following results were obtained with various oils: linseed oil, primary bromine number, 75.7; secondary number, 107.7; wood oil, primary number, 57.0; secondary number, 94.6; earthnut oil, primary number, 52.0; secondary number, 57.6. Non-drying oils do not give a primary bromine number. When calculated into iodine, the secondary or total bromine number of drying oils corresponds closely with the iodine number as estimated directly. The author discusses the relation of the primary and secondary bromine numbers to the composition of the oils.

W. P. S.

Substitution of the Iodine Numbers of Fats by the Bromine Numbers. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1910, 23, 2078—2080).—The author recommends that the bromine numbers of fats and oils be estimated in place of the usual iodine numbers, as the former number is more quickly obtained, and the results are trustworthy. The fat or oil should be dissolved in a somewhat large quantity of carbon tetrachloride, potassium bromide solution and water are then added, the mixture is acidified with hydrochloric acid, and, after the addition of a small crystal of potassium iodide, an excess of potassium bromate solution is introduced. The whole is well shaken in a stoppered flask for one minute, and the excess of bromine is titrated with sodium sulphite solution. The trace of iodine added as iodide serves as the indicator in the titration.

W. P. S.

Analysis of Oils. RENÉ MARCILLE (*Ann. Faleif*, 1910, 3, 417—423).—The author recommends the Wys method for obtaining the iodine numbers of oils in preference to the Hübl method; the results yielded by the latter process vary according to the age of the reagent, the temperature at which the experiment is made, etc. Directions are given for preparing the Wys reagent and for estimating the iodine numbers of oils; the separation of the fluid fatty acids from an oil and the determination of the Tortelli number are also described.

W. P. S.

Halphen's Reaction [for Cottonseed Oil]. LEOPOLD ROSENTHALER (*Zeitsch. Nahr. Genussm.*, 1910, 20, 453—454).—The amyl alcohol used in this test may be replaced by either methyl, ethyl, propyl, isobutyl, benzyl, or allyl alcohols, amylene hydrate (tertiary amyl alcohol), or santalol, but not by aldehydes, ethyl acetate, phytosterol, benzene, phenol, nitrobenzene, aniline, or acetic acid. When cottonseed oil is heated with a solution of sulphur in carbon disulphide, but without the addition of any alcohol, the characteristic coloration is not obtained; if the mixture is heated for a considerable length of time, a faint coloration may be obtained, but this is probably due to partial hydrolysis of the fat with the liberation of glycerol, which latter substance itself, when used in place of amyl alcohol, causes a coloration to be produced after thirty minutes' heating. A faint coloration also develops when ethylene glycol is employed. The solution of sulphur in carbon disulphide cannot be replaced by other sulphur compounds, such as allylthiocarbimide, potassium xanthate, disulphones, etc.

W. P. S.

The Kumawaga-Suto Method of Estimating Fats. YOSHITAKA SHIMIDZU (*Biochem. Zeitsch.*, 1910, 28, 237—273).—The process of drying material which contains water leads to a loss of fat (10% or more), doubtless due to oxidation. The material should therefore be directly saponified by the Kumawaga-Suto method. Illustrative experiments with muscle, liver, blood, etc., are given.

W. D. H.

Method for the Analysis of Fats by the Separation of the Solid Fatty Acids from the Liquid Acids. DAVID (*Compt. rend.*, 1910, 151, 756—757).—The method is based on the observation that the ammonium salts of the solid fatty acids are quite insoluble in large excess of aqueous ammonia at 14—15°, whilst the ammonium salts of the liquid acids are soluble.

A mixture of solid and liquid acids can be separated by dissolving 2 grams in 5 c.c. of warm 95% alcohol; 50 c.c. of pure ammonia are added, and the solution warmed until bubbles of gas begin to be evolved. After remaining several hours at a temperature not exceeding 15°, the liquid is filtered, the ammonium stearate or palmitate washed with ammonia until the filtrate gives no turbidity with barium hydroxide, and then treated on the filter with hydrochloric acid diluted with its own volume of water at 22°. The fatty acids are washed with hydrochloric acid, and finally with water, dried at 100°, and weighed. The experimental error does not exceed 0.2—0.3%.

The process is applicable to mixtures containing other solid acids, such as hydroxystearic, isoleic, lauric, and arachidic acids, and is believed to be of general application.

W. O. W.

The Electrical Conductivity of Milk, and the Use of this Constant for the Detection of Watering and Addition of Electrolytes. RINALDO BINAGHI (*Biochem. Zeitsch.*, 1910, 29, 60—78).—The electrical conductivity of fresh unadulterated milk is approximately a constant for each species. For milk of sheep, $K_{25}(\text{mean}) = 50.40 \times 10^{-4}$; for that of goat, 49.00×10^{-4} ; for cow's milk, 48.70×10^{-4} . The

conductivity diminishes in proportion to the water added. Electrolytes which are added for preservative purposes (borates, etc.) increase the conductivity. The measurement of this constant is recommended for detecting adulteration and addition of preservatives. S. B. S.

The Tests for Purity of Quinine Salts. FRANK TUTIN (*Pharm. Journ.*, 1909, [iv], 29, 600—603).—The methods adopted by the various national pharmacopœias for the detection of impurities in quinine salts are of two kinds: (1) the ammonia test, and (2) specific tests for certain impurities. The author has investigated the effects of various conditions on the results obtained by the application of these two kinds of tests, more particularly as regards the former, and finds that the best method of carrying out the ammonia test is that prescribed in the French Codex, which, however, is only applicable to quinine sulphate. The ammonia test being of limited applicability, the test for cinchonine and cinchonidine prescribed by the British Pharmacopœia is preferable, since it can be used for any quinine salt. The following general conclusions are drawn.

The minimum amount of 10% ammonia solution which will yield a clear solution at 15° with 5 c.c. of a solution of quinine sulphate saturated at 15° is 4.4 c.c., so that it is impossible to meet the requirements of the German Pharmacopœia, which stipulates 4 c.c. of ammonia solution. A reasonable requirement for commercial quinine sulphate would be 6.0 c.c. The quantity of ammonia needed is affected by the alkalinity or acidity of the quinine sulphate used, so that it is not a trustworthy indication of the presence of other alkaloids. In this connexion it is pointed out that solutions of commercial quinine sulphate in water are usually slightly alkaline, and become more so on heating, reverting to their original slight alkalinity on cooling. In applying the ammonia test to quinine salts other than the sulphate, it is usual to convert them into the sulphate in such a way that the test is made in presence of an inorganic salt. The presence of the latter profoundly influences the quantity of ammonia needed, so that the test becomes untrustworthy. For this reason the specific test for cinchonine and cinchonidine prescribed by the British Pharmacopœia is more satisfactory, but in applying it "Aether purificatus," not "Aether," of the Pharmacopœia should be used. The ammonia test is, however, the only one available for the detection of hydroquinine, but it is not yet certain that minute quantities of hydroquinine sulphate are objectionable in quinine sulphate. The specific rotations quoted in the French Codex for several quinine salts are not in harmony with each other, and could not be confirmed.

The following new salts were prepared: Quinine d-camphor-sulphonate, m. p. 191°, colourless needles from water or dilute alcohol. Quinine d-bromocamphorsulphonate, m. p. 260° (decomp.), crystalline from dilute alcohol, but is insoluble in water. Hydroquinine d-camphor-sulphonate, m. p. 217—218°, and d-bromocamphorsulphonate, m. p. 266°, are both crystalline. T. A. H.

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- γ -Dimethylamino- α -*p*-nitrophenoxy-
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 Catalase.
 Cellase.
 Chymosin.
 Diastase.
 Emulsin.
 Enterolipase.
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 Glycogenase.
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 Hedera-peroxylase.
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- α -Phenyl- β -anisyl- $\Delta\alpha$ -butene- γ^2 -dianil** (BORSCH and TITSINGH), A., i, 66.
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- α -Phenyl- β -di-*p*-ethylphenylpropionic acid, and its ethyl ester (BISTREZCKI and MAURON), A., i, 845.
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- 2-Phenyldihydroindole, methiodide of (SCHOLTZ and WOLFRUM), A., i, 772.
- 7-Phenyldihydro- α - β -phenanthracene, 10-hydroxy-, and its acetyl derivative (POPE and HOWARD), T., 976.
- 3-Phenyldihydropyrazoloquinazoline, 6-amino-, and its benzylidene derivative, 4:6-dichloro-, and 6-oximino- (MICHAELIS and LEO), A., i, 515.
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- 1-Phenyl-2:4-dimethyl-3-hydroxy-methylpyrazolenedi- α -acetic acid, *p*-amino- (FARBERKE VORM. MEISTER, LUCIUS, and BRÜNING), A., i, 340.
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- β -Phenyl- α -dimethylpropionyl chloride (HALLER and BAUER), A., i, 490.
- 1-Phenyl-2:3-dimethyl-5-pyrazolones, soluble compounds from (RIEDER), A., i, 433.
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- 1-Phenyl-3-ethoxymethyl-5-pyrazolone-4-carboxylic acid, *p*-nitro-, ethyl ester (FARBWERKEFORM. MEISTER, LUCIUS, & BRÜNING), A., i, 340.
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- α*-Phenyl-*α*-ethylbutyramide (BODROUX and TABOURY), A., i, 557.
- α*-Phenyl-*α*-ethylbutyric acid (BODROUX), A., i, 672.
- α*-Phenyl-*α*-ethylbutyronitrile (BODROUX and TABOURY), A., i, 482.
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- 3-Phenyl-6-ethylidihydropyrazoquinazoline (MICHAELIS and LEO), A., i, 516.
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- Phenylethylmethylamine, *p*-hydroxy-, and its derivatives (WALPOLE), T., 945; P., 88.
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- p*-nitro-, and its hydrobromide (JOHNSON and GUEST), A., i, 471.
- γ*-Phenyl-*γ*-ethylpentane (SCHREINER), A., i, 661.
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- β*-Phenyl-*α*-ethylpropionophenone, and its oxime (HALLER and BAUER), A., i, 490.
- Phenylethylpropylamine, 3:4-dihydroxy-, and its hydrochloride (PYMAN), T., 275.
- Phenylethylthiobenzamide (RUSSELL), T., 957.
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- 9-Phenylfluorene-9-carboxylic acid, *p*-hydroxy-, and lactone of *o*-hydroxy- (BISCHOFF and v. WEBER), A., i, 749.
- 9-Phenylfluorene, tetrabromo-3-hydroxy- (POPE and HOWARD), T., 82.
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- Phenylformylaminomethylcarbinol (PICTET and GAMS), A., i, 774.
- Phenylfumardiamide, *p*-hydroxy- (PICTET), A., i, 23.
- 1-Phenyl-5-furyl-3-methylpyrazoline (AUWERS and VOSS), A., i, 71.
- 1-Phenyl-3-furyl-2-methyl-5-isopyrazolone, 4-nitroso-, and its hydrochloride (TORREY and ZANETTI), A., i, 893.
- 1-Phenyl-3-furyl-5-pyrazolone, hydrochloride, and *p*-bromo-, *m*-nitro-, and 4-oximino- (TORREY and ZANETTI), A., i, 893.
- 2-Phenyl-3-furyl-4-isopyrazolone (TORREY and ZANETTI), A., i, 893.
- 1-Phenylgeraniol (AUSTERWEIL and COCHIN), A., i, 637.
- β*-Phenylglutamic acid and its barium and calcium salts, semi-anilide, semi-*p*-tolimide, anil and *p*-tolil (FEIST and FOXME), A., i, 39.

- β -Phenylglutaric acid**, $\alpha\beta$ -dibromo- (FRIST and POMME), A., i, 39.
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- α - and γ -Styryl nonyl ketone**, derivatives of (SCHOLZ and MEYER), A., i, 562.
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- $\text{C}_4\text{H}_5\text{O}_2\text{N}_3$, from α -methazonic anhydride and water (STEINSKOPF, BOHRMANN, GRÜNPPF, KIRCHHOFF, JÜRGENS, and BENEDEK), A., i, 808.
- $\text{C}_4\text{H}_5\text{N}_2\text{S}_2$, from diguanide and carbon disulphide (RACKMANN), A., i, 827.
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- $\text{C}_4\text{H}_5\text{O}_2\text{N}_3$, from triazomethylcarbimide and water (FORSTER and MÜLLER), T., 1063.
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- $\text{C}_4\text{H}_5\text{O}_2\text{N}$, from α -aminoglutaric acid, aurichloride of (ENGELAND), A., i, 843.
- $\text{C}_4\text{H}_5\text{O}_2\text{SHgNa}$, from hydroxymercurybenzoic anhydride and sodium sulphite (SCHÖZLER and SCHRAUTH), A., i, 460.
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- Substance, $C_8H_{17}N$** , reduction product of η -chloro-octylamine and its salts (GABRIEL), A., i, 229.
- $C_8H_9O_2N_3$, from aniline and nitroacetonitrile (STEINKOPF, BOHRMANN, GRUNUPP, KIRCHHOFF, JÜRGENS, and BENEDEK), A., i, 307.
- $C_{10}H_{10}O_2N_2$, from phenyltriazomethyl-carbamide and sodium carbonate (FORSTER and MÜLLER), T., 1065.
- $C_{10}H_{10}O_2N_4$, from 4:5-diamino-2:6-di-keto-1:3-dimethylpyrimidine (FARBENFABRIKEN VOHM, F. BAYER & Co.), A., i, 79.
- $C_8H_{11}O_2N_2$, from acetonecyanohydrin and hydrogen chloride (ULTEE), A., i, 15.
- $C_8H_5ON_2K$, from p -triazobenzaldehyde and potassium cyanide (FORSTER and JUDD), T., 260.
- $C_8H_7O_3$, from nonaldehyde and ozone (HARRIES and KOETSCHAU), A., i, 607.
- $C_8H_{11}O_2$, additive compound of quinol and acetone (SCHMIDLIN and LANG), A., i, 837.
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- $C_8H_{12}O_7$, from the interaction of ethyl malonate, sodium ethoxide, and iodine (KOMNENOS), A., i, 542.
- $C_8H_{12}O_9$, from oxidation of 1:3-dimethyl-5-methylene- Δ^2 -cyclohexene (ATWERS and PETERS), A., i, 826.
- $C_8H_5O_2N_2$, from 1-chloro-2:4-dinitrobenzene and sodioacetone (REITZENSTEIN and STAMM), A., ii, 358.
- $C_8H_5OS_2$, from acetophenone and carbon disulphide, and its derivatives (KELBER), A., i, 391.
- $C_8H_{11}O_4N$, from coal tar (SCHULTZ and SZÉKELY), A., i, 725.
- $C_9H_{11}O_2N_3$, from α -toluidine and nitroacetonitrile (STEINKOPF, BOHRMANN, GRUNUPP, KIRCHHOFF, JÜRGENS, and BENEDEK), A., i, 307.
- $C_8H_{17}O_2N$, from α -aminoglutaric acid, auri-chloride of (ENGELAND), A., i, 843.
- $C_{10}H_{12}O$, from polymeric of crotonaldehyde (DELÉPINÉ), A., i, 219.
- $C_{10}H_{18}Cl_2$, from isothylene (KONDAKOFF and SKWORZOFF), A., i, 755.
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- Substance, $C_{10}H_2O_2N_4$** , from α -methazonic anhydride (STEINKOPF, BOHRMANN, GRUNUPP, KIRCHHOFF, JÜRGENS, and BENEDEK), A., i, 308.
- $C_{10}H_{11}O_2N_3$, from methyl 1-phenyl-5-triazolone-4-carboxylate and alcoholic hydrogen sulphide (DIMROTH, ARKELIN, BRAUN, FESTER, and MERCKLE), A., i, 519.
- $C_{10}H_7O_2N_3$, from 4-keto-2-benzyl-4:5-dihydroglyoxaline and water (FINGER and ZER), A., i, 591.
- $C_{10}H_{12}O_2N_3$, from m -xylydine and nitroacetonitrile (STEINKOPF, BOHRMANN, GRUNUPP, KIRCHHOFF, JÜRGENS, and BENEDEK), A., i, 307.
- $C_{10}H_7O_2N_3$, isomeride of α -limonene-hydroxylamineoxime (CUSMANN), A., i, 686.
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- $C_{11}H_{13}O_3$, from ethylmethylacetonedicarboxylate (FEIST and POMME), A., i, 9.
- $C_{11}H_9O_2N_3$, from pyridine and 1:3-dichloro 4:6 dinitrobenzene, salts of (ZINCKE and WEISFENNING), A., i, 585.
- $C_{11}H_{15}O_2N$, from action of sodium hydride on cyanacetone (CLARKE and LAPWORTH), T., 15.
- $C_{11}H_{20}O_2N_3$, from 4-methylamino-1:2:2:4-dimethyl-5-pyrrolidone and ethylene oxide (KOH and BUN), A., i, 137.
- $C_{11}H_7O_2S_2$, from dimethyl ether of $C_4H_5OS_2$ (KELBER), A., i, 391.
- $C_{11}H_7O_2HS_2$, from dimethyl ether of $C_4H_5OS_2$ (KELBER), A., i, 391.
- $C_{12}H_{11}$, from action of silent electric discharge on benzene and hydrogen (LOSANTSCH), A., i, 2.
- $C_{12}H_7O$, from acenaphthenequinone, and its magnesium salts (KALLÉ & Co.), A., i, 752.
- $C_{12}H_7O_2$, additive compound of phenol and cyclohexanone (SCHMIDLIN and LANG), A., i, 837.
- $C_{12}H_7O_4$, additive compound of resorcinol and acetone (SCHMIDLIN and LANG), A., i, 837.
- $C_{12}H_{22}O$, from lauryl chloride by the action of heat (BISTEZZONI and LANZUING), A., i, 87.
- $C_{12}H_{20}O_2$, from polymeric of crotonaldehyde (DELÉPINÉ), A., i, 219.
- $C_{12}H_8O_2S_2$, from oxidation of diphenylene p disulphoxide (+ $2H_2O$), (HILDTICH), T., 2588.

- Substance, $C_{12}H_{19}O_2N_3$, from betaine, $C_2H_5O_2N_3$, and sodium hydroxide (ZINCKE), A., i, 556.
- $C_{12}H_{19}O_2N_3$, from the action of nitrous acid on ethyl 1-imino-hydrindene-2-carboxylate (MITCHELL and THORPE), T., 2272.
- $C_{12}H_{13}O_2N$, oxime from ethyl tetrahydrobenzenedicarboxylate (LEUCHS and THEODORESCU), A., i, 396.
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- $C_{12}H_{19}O_2N_3$, from the action of nitrous acid on the β -condensation product of *m*-4-xyldine and acetaldehyde (JONES and WHITE), T., 642.
- $C_{12}H_{13}OI$, from phenoxyhexylene (DIONNEAU), A., i, 354.
- $C_{12}H_{13}O_2N_4$, from hexamethylene-tetramine and resorcinol (GRISKE-WITSCH-TROCHIMOWSKY), A., i, 103.
- $C_{12}H_{19}O_2N$, condensation product from acetonecyanohydrin and hydrogen chloride (ULIÉ), A., i, 15.
- $C_{12}H_{19}O_{12}N$, from the nitration of cellulose (CHANE and JOYCE), A., i, 364.
- $C_{12}H_{19}O_2N_2Na$, from oxidation of aniline-*p*-sulphonic acid (REIFENSTEIN), A., i, 703.
- $C_{12}H_{19}O_2$, from the condensation of cyclobutan-1,3-dione in the presence of quinoline (CHICK and WILMORE), T., 1993; P., 217.
- $C_{12}H_{12}O_4$, from oxypucedanin by the action of sulphuric acid (HERZOG and KROHN), A., i, 125.
- $C_{12}H_{12}N_2$, from dehydracetic acid (BENARY), A., i, 135.
- $C_{12}H_{14}O_3$ and its acetyl derivative and phenylmethane, from oxypucedanin (HERZOG and KROHN), A., i, 125.
- $C_{12}H_{19}O_2$, from α -cyclogeraniol (BOUVEAULT), A., i, 380.
- $C_{12}H_{13}O_2N_2$, from ethyl α -cyano- α -ketobutyrate phenylhydrazones (WISLICENUS and SILBERSTEIN), A., i, 539.
- $C_{12}H_{19}ON$, α - and β -isomerides from ψ -cavidine and acetaldehyde (JONES and WHITE), T., 643.
- $C_{12}H_{18}O_2N_2$, from 4-ethylamino-2:2:3-trimethyl-1-ethyl-5-pyrrolidone and ethylene oxide (KOH and BUM), A., i, 137.
- $C_{12}H_{19}O_2N_2S$ and its methyl ester (MAYER), A., i, 261.
- Substance, $C_2H_3O_3NI_3$, from di-iodotyrosine, methyl iodide and potassium hydroxide (WHEELER and JOHNS), A., i, 114.
- $C_{11}H_{12}O_6$, from extract of red clover flowers (POWER and SALWAY), T., 243; P., 29.
- $C_{11}H_{12}O_6$, from isogalloflavin trimethyl ether (HERZIG, ERDÖS, and RIZICKA), A., i, 676.
- $C_{11}H_{11}O_6$, from α -dimethylglutamic acid and phosphorus pentachloride, and its anilide and methyl hydrogen ester (FEIST and REUTER), A., i, 10.
- $C_{11}H_{12}ON_2$, from salicylideneaniline and potassium cyanide (ROHR and SCHÄTEL), A., i, 776.
- $C_{11}H_{19}O_2N_2$, from 4-keto-2-benzyl-4:5-dihydroglyoxaline (FINGER and ZEH), A., i, 591.
- $C_{11}H_{19}O_2N_2$, from ethyl 1-cyanocyclopropane-1-carboxylate (MITCHELL and THORPE), T., 1001.
- $C_{11}H_{14}O_2Br_2$, from $C_{11}H_{11}O_2$ and bromine (FEIST and REUTER), A., i, 10.
- $C_{11}H_{17}O_2N$, from *p*-ethoxyphenylmalonimide and its sodium derivative (PUTTI), A., i, 23.
- $C_{11}H_{11}O_2N_2Cl$, from nitrosobenzene and methyl 5-chloroanthranilate (FREUNDLICH), A., i, 446.
- $C_{11}H_{12}O_2NCl_2$, from carpine hydrochloride and chlorine (BARGER), T., 172; P., 53.
- $C_{11}H_{15}O_2NCl_2Sh$, from di-*p*-anisylamine and antimony pentachloride (WIELAND and WICKER), A., i, 243.
- $C_{11}H_{16}O_6$, from extract of red clover flowers and its acetyl derivative (POWER and SALWAY), T., 239; P., 20.
- $C_{11}H_{14}O_3$, condensation product of catechol and acetone (SCHMIDLIN and LANG), A., i, 837.
- $C_{11}H_{16}O_2$, from isogalloflavin trimethyl ether (HERZIG, ERDÖS, and RIZICKA), A., i, 677.
- $C_{11}H_{15}O_3$, additive compound of phenol and acetone (SCHMIDLIN and LANG), A., i, 837.
- $C_{11}H_{12}O$, from the essential oil of hyacinths (ENKLAAR), A., i, 123.
- $C_{11}H_{12}O_6$, from action of sodium methoxide on $C_{11}H_{11}O_5$ (FEIST and REUTER), A., i, 10.
- $C_{11}H_{12}O_6$, from rhizome of *Cimicifuga racemosa* (FINNEMORE), A., ii, 891.
- $C_{11}H_{12}O_6$, additive compound of acetone and pyrogallol (SCHMIDLIN and LANG), A., i, 837.

- Substance, $C_{15}H_{20}O$, from diethyl ketone and methyl iodide (HALLER and BAUER), A., i, 300.
- $C_{15}H_{19}O_2N$, from phenylhydroxylamine and benzoylacetalddehyde (ALESSANDRI), A., i, 753.
- $C_{10}H_{12}ONS$, from aniline and a substance from acetophenone (KELBER), A., i, 391.
- $C_{15}H_{15}ON_3S$, from 5-thion-1:4-diphenyltriazole (NIRDLINGER and ACREE), A., i, 786.
- $C_{15}H_{19}O_3N_3K_3$, from s-trinitrobenzene and potassium propoxide (BUSCH and KÜGEL), A., i, 474.
- $C_{17}H_{25}ONCl_2Fe$, ferrichloride of the additive compound of tropine and benzyl chloride (SCHOLTZ), A., i, 97.
- $C_{15}H_{15}O_2$, from extract of red clover flowers and its acetyl derivative (POWER and SALWAY), T., 236:P. 20.
- $C_{16}H_{18}O_9$, from isogalloflavin trimethyl ether (HERZIG, ERDÖS, and RUZICKA), A., i, 678.
- $C_{16}H_{20}O$, from action of silent electric discharge on ethylene (LOSANTICH), A., i, 1.
- $C_{16}H_{12}O_2S_2$, from oxidation of "thio-indigo" (DANAÏLA), A., i, 411.
- $C_{16}H_{12}O_2S_2$, from oxidation of "thio-indigo" (DANAÏLA), A., i, 411.
- $C_{16}H_{12}O_2S_2$, from oxidation of "thio-indigo" (DANAÏLA), A., i, 411.
- $C_{16}H_{17}O_2N_3$, from picryl- α -naphthylamine and silver oxide (BUSCH and KÜGEL), A., i, 473.
- $C_{16}H_{11}O_7N_3$, from 3:5-dinitro-4-hydroxybenzoic acid and quinoline (MORGENSTERN), A., i, 483.
- $C_{16}H_{15}O_2N$, from safrole and nitrosobenzene, 2 isomerides (ANGELL, ALESSANDRI, and PEGNA), A., i, 552.
- $C_{16}H_{15}O_2N$, from chrysopaenic acid methyl ether and ammonia (+ $\frac{1}{2}H_2O$) (OSTERLE and JOHANN), A., i, 860.
- $C_{16}H_{17}O_3N_3$, from dinitrophenyldipyridinium dichloride and alkali, and its salts (ZINCKE and WEISFENNING), A., i, 585.
- $C_{17}H_{21}O_2N$, from dimethylketen and benzylidenemethylamine (STAUDINGER, KLEFFER, and KOEHL), A., i, 588.
- $C_{16}H_{21}O_8P$, from pierotin and phosphorus pentachloride (HORMANN), A., i, 577.
- $C_{18}H_{14}ON_2S$, condensation product of 3-oxyl-1-thionaphthen with p -nitrosodimethylaniline (BADISCHE ANILIN- & SODAFABRIK), A., i, 60.
- Substance, $C_{16}H_{10}O_4N_2S_2Na_2$, from 1-naphthol-4-sulphonic acid, phenylhydrazine and sodium hydrogen sulphite (BUTCHER and SONNENBERG), A., i, 145.
- $C_{17}H_{16}N_2$, from interaction of magnesium phenyl bromide and 3:3-dimethylindoline-2-carboxylonitrile, and its oxime and p -nitrophenylhydrazine (PLANCHER and GEMELLI), A., i, 53.
- $C_{17}H_{16}O_2N_2$, from 3:5-dinitro-4-hydroxybenzoic acid and naphthalene (MORGENSTERN), A., i, 482.
- $C_{17}H_{17}O_2Br_2$, from the reduction of β -bromocarmine (ROHDE and DORMEIER), A., i, 492.
- $C_{17}H_{22}O_2N_2$, from α -leucyl-L-tryptophan (FISCHER), A., i, 22.
- $C_{17}H_{26}O_2Cl_4$, from fatty acids in cod liver oil (HEIDESCHKA and RHEINBERGER), A., i, 297.
- $C_{17}H_{19}O_2N_2Cl$, from picryl chloride and methyl- α -naphthylamine (BUSCH and KÜGEL), A., i, 473.
- $C_{17}H_{14}O_2N_2S_2$, from immedial-indone (FRANK), T., 2045; P., 218.
- $C_{17}H_{19}N_2Cl_2Hg_2$, from dinitrophenylpyridinium chloride and p -aminophenyl mercuriacetate (REITZENSTEIN and STAMM), A., i, 313.
- $C_{17}H_{22}O_2Cl_4$, from fatty acids of cod liver oil (HEIDESCHKA and RHEINBERGER), A., i, 297.
- $C_{17}H_{17}O_2BrMg$, from action of magnesium on p -tolyl ethyl ketone and allyl bromide (GRISHKEWITSCH-TROCHIMOVSKY), A., i, 109.
- $C_{17}H_{19}ON_2Cl_2Hg_2$, from dinitrophenylpyridinium chloride and p -aminophenyl mercuriacetate (REITZENSTEIN and STAMM), A., i, 313.
- $C_{18}H_{20}O_8$, from kermesic acid and hydriodic acid (DINBOOTH), A., i, 458.
- $C_{18}H_{16}O_6$, from 3-hydroxymethylfluorene (KEHRMANN and JONES), A., i, 409.
- $C_{18}H_{20}O_9$, from isogalloflavin trimethyl ether (HERZIG, ERDÖS, and RUZICKA), A., i, 678.
- $C_{19}H_{21}O_2N$, from ester, $C_{20}H_{23}O_2N$ (WILLGROEDT and MAFFEZOLI), A., i, 679.
- $C_{18}H_{17}O_2S_2$, from $C_{16}H_{12}O_2S_2$ and ammonium persulphate (KELBER), A., i, 391.
- $C_{19}H_{14}O_2N_2$, from isobenzylglyoxalidone and sodium hydroxide (FINGER and ZEN), A., i, 591.
- $C_{18}H_{16}O_2N_2$, from ethylengonol and nitrosobenzene (ANGELL, ALESSANDRI, and PEGNA), A., i, 553.

- Substance, $C_{10}H_{12}O_2N_2$, from hexamethylenetetramine and catechol (GRISHKEWITSCH-TROCHIMOWSKY), A., i, 108.
- $C_{16}H_{12}O_4$, from 3-phenylpyrazoisocoumarazone and resorcinol (MICHAELIS and LEO), A., i, 516.
- $C_{18}H_{14}O_2$, from 3-methylpyrazoisocoumarazone and resorcinol (MICHAELIS and LEO), A., i, 516.
- $C_{19}H_{28}O_{10}$, from biliary acids (PREGL), A., i, 321.
- $C_{10}H_{14}O_2N_2$, from 3:5-dinitro-4-hydroxybenzoic acid and acenaphthene (MORGENTERN), A., i, 482.
- $C_{19}H_{16}O_4Cl_2$, from 2:5-dihydroxytriphenylcarbinol (V. BAeyer, AICKELIN, DIEHL, HALLENSLEDEN, and HESS), A., i, 219.
- $C_{18}H_{12}O_2N_2$, from *p*-benzoquinone and diaminodiphenylmethane (SIEGMUND), A., 749.
- $C_{19}H_{12}N_2ClHg$, from 3-mercury-*p*-toluidine and dinitrophenylpyridinium chloride (REITZENSTEIN and STAMM), A., i, 348.
- $C_{20}H_{20}O_2$, from methyl chloroformate and ostruthin (HEERZOG and KROHN), A., i, 125.
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